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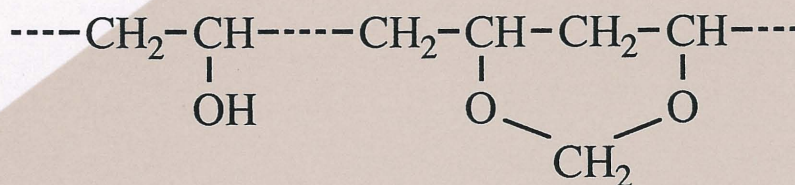
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***ICR***

# ANNUAL REPORT

**1995**



VINYLON

**Kyoto University  
Institute for Chemical Research**



**Volume 2**



**ICR ANNUAL REPORT 1995 (Volume 2)**

For the calendar year 1 January 1995 to 31 December 1995

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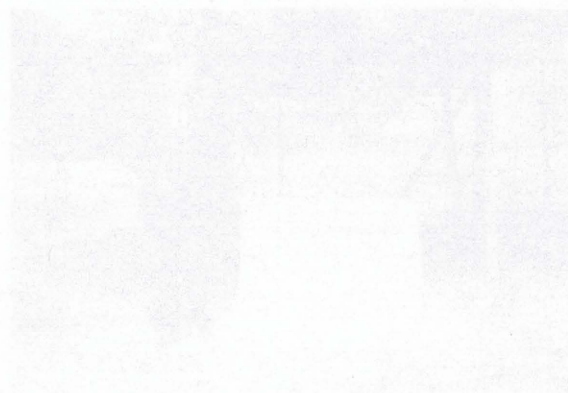
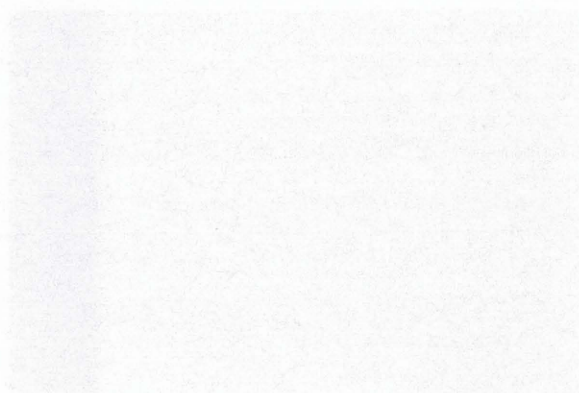
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31 March 1996

**I C R**

# **ANNUAL REPORT 1995**



**Kyoto University  
Institute for Chemical Research**

**Volume 2**

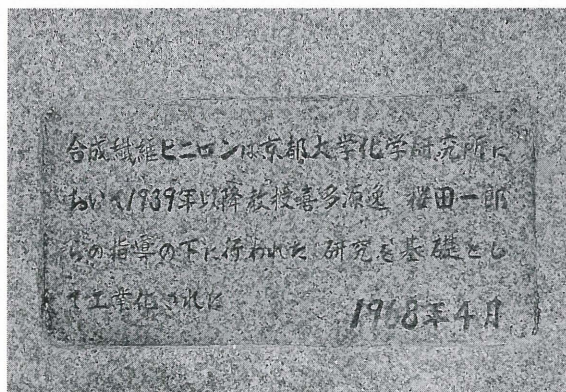
**Front cover:** *Historical remarks to the Institute for Chemical Research (ICR)*

The chemical structure shown on the front cover represents poly(vinyl alcohol) (PVA) fiber, which was given the general name "vinylon" in Japan in 1948; later it was named "vinal" in the United States. Ichiro Sakurada and his collaborators succeeded in preparing water-insoluble PVA fiber, named "Kasen Gosei Ichigo [化繊合成一號]" meaning "Chemical Fiber, Synthesis No. 1 in Japan", in 1939 at the Institute for Chemical Research, Kyoto University. This was done by wet spinning of an aqueous solution of PVA into a coagulation bath of a sodium sulfate solution, and by subsequent formalization of the fiber. The chemical structure indicated corresponds to this fiber; in the structure of alternation of crystalline and amorphous regions only the amorphous parts are formalized. In 1940 they succeeded in improving the hot-water resistance of the fiber by means of heat

treatment of the wet-spun fiber in hot air, and by a suitable combination of heat treatment and formalization fiber could be obtained that was insoluble and stable without shrinkage even in boiling water. The pilot plant for developmental work on this fiber was erected in 1942 on the campus of this Institute, Takatsuki, Osaka (at that time), through the support of the semigovernmental organization, The Foundation for Synthetic Fiber Research, Japan. The test operation of this plant was continued during World War II and brought about great advances in expertise in the manufacturing process. Soon after the end of the War, a great effort to establish an industrial process for this fiber was made, and commercial production started in 1950. (Further reading: "Polyvinyl Alcohol Fibers" by I. Sakurada, Marcel Dekker, 1985.)



**Photo. 1** Professor Ichiro Sakurada stands by the Monument for the Invention of Vinylon Fiber



**Photo. 2** The inscription on the Monument :  
The synthetic fiber "VINYLON" was industrialized based on the fundamental investigations which had been conducted under the guidance of Prof Gen-itsu Kita and Prof Ichiro Sakurada at the Institute for Chemical Research, Kyoto University since 1939.

April 1968



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## Preface

Last year we published the first issue of the *ICR* Annual Report to widely distribute the current activities of *ICR* including the Abstracts of selected papers, details of publications and the organization of the laboratories. This is the 1995 edition of the *ICR* Annual Report.

Currently, there are approximately 100 full-time members of staff, 200 graduate students including 20 foreign students, and 25 domestic researchers working in *ICR*. During the calendar year of 1995, 370 papers were published by the members of *ICR* and we received 68 foreign visiting scientists. Six big high-performance apparatus were newly installed, which were 600MHz and 400MHz FT-NMR, Photoelectron Spectrometer (PES), Tandem and High-resolution Mass Spectrometers and ESR Spectrometer. The present Super-Computer System will be replaced with a higher class one this year.

As for changes in staff, Prof. Nobuyuki Sugita at the High-Pressure Organic Chemistry Laboratory retired at the end of March in 1995, and Dr. Koichi Komatsu was promoted to full Professor of the Laboratory on April 1, 1995. Prof. Kenji Soda at the Molecular Microbial Science Laboratory will retire at the end of March in 1996. On the other hand, there were many large accidents in the country. Among them is the Hanshin-Awaji Earthquake, which struck Kobe on January 17, 1995 and gave us many lessons. Fortunately the Institute, situated about 60 km from the epicenter, had no serious damage. However, it reminded us of the importance of considering counterplans for earthquakes, since we have various types of, and large amounts of inflammable chemicals in stock.

It is a great pleasure to write this preface for the *ICR* Annual Report, the last one I shall write. Prof. Teruya Shinjo was appointed new Director of *ICR* from April 1, 1996. The *ICR* now became 70 years old, and will celebrate its 70th anniversary in November this year. I am confident that this occasion and the years to come will witness the flourishing achievement of *ICR*'s scientific activities under a new leadership. I also hope that this Annual Report will continue to play an important role in promoting a number of domestic as well as international collaborations.



Takeaki Miyamoto  
DIRECTOR





**TOPICS AND INTRODUCTORY COLUMNS  
OF LABORATORIES**



# Ionic and Covalent Bonds in $\text{CeO}_2$ Crystal

Hirohide Nakamura and Takeshi Mikiyama

The ionic and covalent bonds in  $\text{CeO}_2$  crystal were studied by means of the X-ray photoelectron spectroscopy (XPS) and the infrared spectroscopy (IR). The XPS spectra of  $\text{CeO}_2$  crystal showed the presence of the ionic bonds between the  $\text{Ce}^{4+}$  and  $\text{O}^{2-}$  ions. The IR spectra of  $\text{CeO}_2$  crystal showed the presence of the covalent bonds between the  $\text{Ce}^{4+}$  and  $\text{O}^{2-}$  ions. The results of the XPS and IR spectra are discussed in terms of the ionic and covalent bonds in  $\text{CeO}_2$  crystal.

**Keywords:** Bond nature; Lanthanum;  $\text{CeO}_2$ ; Electron; electronic structure; Bond; X-ray photoelectron spectroscopy; Infrared spectroscopy

## Key to headline in the columns

### RESEARCH DIVISION—Laboratory (Subdivision)\*

\* See also "Organization and Staff" on page 87.

## Abbreviations used in the columns

Prof	Professor	GS	Graduate Student
Vis Prof	Visiting Professor	DC	Doctor's Course (Program)
Assoc Prof	Associate Professor	MC	Master's Course
Lect	Lecturer	UG	Undergraduate Student
Lect (pt)	Lecturer (part-time)	RF	Research Fellow
Instr	Instructor	RS	Research Student
Assoc Instr	Associate Instructor		
Techn	Technician	D Sc	Doctor of Science
Guest Scholar	Guest Scholar	D Eng	Doctor of Engineering
Guest Res Assoc	Guest Research Associate	D Agr	Doctor of Agricultural Science
Univ	University	D Pharm Sc	Doctor of Pharmaceutical Sciences
		D Med Sc	Doctor of Medical Science



# Ionic and Covalent Bonds in CeO<sub>2</sub> Crystal

Hirohide Nakamatsu and Takeshi Mukoyama

We have performed cluster calculations to study the bonding nature in the CeO<sub>2</sub> crystal, using the relativistic discrete-variational X $\alpha$  method. The electron charge distribution of CeO<sub>2</sub> is compared with those of ZrO<sub>2</sub> and CaF<sub>2</sub>. The charge density in the metal atomic region indicates stronger covalency for CeO<sub>2</sub> than that in Zr for ZrO<sub>2</sub>. The repulsion between the metal and oxygen ionic cores is, however, strong and superior to the covalent interaction, and thus the ionic character determines the static bonding nature in the CeO<sub>2</sub> crystal. Mixed interaction due to the independent ionic and covalent contributions arises from the ionic Ce 5s, 5p and covalent Ce 4f, 5d orbitals which are proximate to each other in the bond region.

**Keywords:** Bond nature/ Lanthanoid/ ZrO<sub>2</sub> / CaF<sub>2</sub> / Relativistic electronic structure/ Dirac-Fock-Slater method

Like alkaline earth metals, lanthanoids have a primary character of hard ionic spheres in solutions and insulators. In particular, 4f orbitals were not considered to be a participant in chemical bonding because they are smaller in size than the filled 5p orbitals and the 4f energy bands of compounds are generally narrow due to a small ligand field. Contrary to typical ionic behavior, the 4f and 5d orbitals of lanthanoids are considered to participate significantly in covalent bonding according to the electronic structure calculations. Koelling et al. deduced the presence of f and d covalent bonding in CeO<sub>2</sub> and PrO<sub>2</sub> from band calculations(1).

Gschneidner has shown that the 4f electron concentration in the bonding is estimated to be about 0.7 of an electron for light lanthanoids by an analysis of the melting point and heat of sublimation for the met-

als(2). A summary of the experimental work concerning the participation of 4f orbitals in the chemical bonding is presented in Ref. 2. Photoelectron spectra and X-ray absorption spectra indicate 4f participation in the bonding of Ce compounds. However, the relation between the analyzed covalent character and the typical ionic behavior in insulator materials has not been clearly revealed.

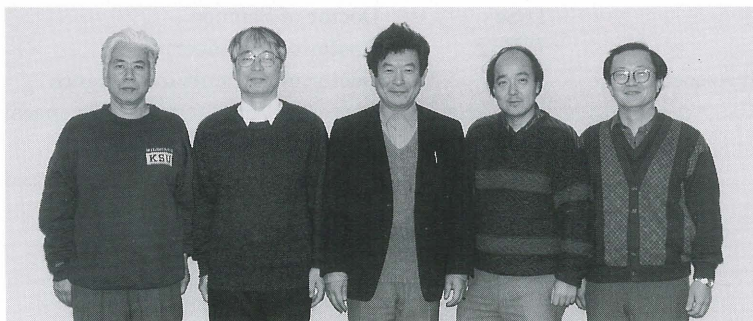
In the present work(3), relativistic DV-X $\alpha$  calculations for CeO<sub>2</sub>, CaF<sub>2</sub> and ZrO<sub>2</sub> compounds have been performed to clarify the ionic bond and the covalent one due to the lanthanoid 4f and 5d orbitals.

Relativistic calculations are indispensable to the study of the electronic structure of molecules containing heavy elements. It has been shown that relativistic effects play a substantial role in the chemical

## STATES AND STRUCTURES —Atomic and Molecular Physics—

### Scope of research

*In order to obtain fundamental information on the property and the structure of materials, the electronic states of atoms and molecules are investigated in detail using X-ray, SR, ion beam from accelerator and nuclear radiation from radioisotopes. Theoretical analysis of the electronic states and development of new radiation detectors are also performed.*



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bonding of atoms with an atomic number greater than 50(4). In particular, the f orbitals in question are remarkably changed in energy and spatial distribution due to the relativistic effect(5). In the present work, we performed relativistic DV-X $\alpha$  calculations based on the Dirac-Fock-Slater method and the cluster model was used for compounds.

The electron charge density calculated for the clusters is examined. The charge densities of valence bands with O 2p and F 2p as the main components are studied since the covalent interaction appears in these bands. The other occupied bands make small contributions to the covalent bonding. The metal ions share the charge density of the O 2p and F 2p valence bands according to the covalency. For CaF<sub>2</sub>, a typical ionic compound, the F 2p component essentially determines the charge distribution and the contribution from the Ca component is negligibly small. The peak at the Ca nucleus is present but its radially integrated quantity within the atomic sphere is negligible. In the case of ZrO<sub>2</sub>, which is considered to have a strong covalent character among the various types of metal oxides, a large contribution of the Zr orbitals to the "O 2p band" is clarified in this charge density plot. For CeO<sub>2</sub>, the participation of the Ce orbitals into the valence state is found to be remarkable and the metal atom component is greater than that of the Zr oxides. The covalent interaction between the Ce and O ions produces the charge density for the Ce 4f and 5d orbitals in the O 2p band. The charge density in the interatomic region around  $r = 2a_u$  is lower for CeO<sub>2</sub> than that for ZrO<sub>2</sub>, though the charge density inside the Ce atom is larger than that inside Zr.

A precise examination of the charge density in the interatomic region and the population analysis lead to the conclusion that the ionic bonding is the determinant of the chemical bonding in CeO<sub>2</sub> at the equilibrium interatomic distance even though the covalency is strong in the sense of orbital participation in forming the valence state. These independent ionic and covalent interactions arise from the ionic 5s, 5p and covalent 4f and 5d orbitals which are proximate to each other with respect to the energy and amplitude of the wavefunction in the bond region.

The ionic and covalent characteristics have been investigated by observing the charge density distribution for the valence bands of CaF<sub>2</sub> and ZrO<sub>2</sub>. For CeO<sub>2</sub>, the charge density in the bond region between the Ce and O atoms is almost equal to that of the ideal ion. This implies that the Ce and O atoms are joined with the ionic bond, whereas the charge density within the Ce atomic region indicates a stronger

covalent interaction than that for ZrO<sub>2</sub>. This *mixed interaction* due to the independent ionic and covalent contributions arises from the Ce 5s, 5p, 4f and 5d orbitals which are proximate to each other in the bond region. The components of Ce 5s, 5p make a repulsive interaction with O 2p because of overlap of the essentially filled orbitals. Concerning the bonding in CeO<sub>2</sub>, this repulsion cancels the covalent bonding between Ce 4f, 5d and O 2p. The present result mentioned is valid at the equilibrium interatomic distance.

The effective charges of the Ce and O ions are notably reduced owing to the covalent interaction, but they do not reflect the strength of the actual covalent bond which lies in the interatomic region on the bond axis. In contrast to CeO<sub>2</sub>, for most of the insulator compounds consisting of light elements including some transition metals, the deviation of the effective charge from that of the ideal ion can be a useful measure of the charge density contributing to the covalent bonding. This measure postulates that the overlap between two hybrid orbitals is enough to characterize the covalent bonding. In a simple case, the hybrid orbital of each atom consists of a single atomic orbital. Actually, the bonding in ZrO<sub>2</sub> is characterized by a pair of Zr 4d and O 2p. They effectively make a covalent contribution to the bond. In the case of CeO<sub>2</sub>, several kinds of Ce valence orbitals are concerned with the bonding characteristics and form an *overlap complex* where various kinds of independent orbital overlaps are significant. This really includes a direct overlap of the ionic cores which produces the repulsive interaction. The effective charge of the Ce ion is small relative to the formal charge, because both the Ce 4f and 5d orbitals participate in sharing the charge in the valence bands. Moreover, the Ce 5s, 5p components cause the repulsion of the ionic cores and are the determinant of the dominant ionic nature.

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# Quantitative Energy-Filtering Image of Carbon Nanotube

Hiroki Kurata, Seiji Isoda and Takashi Kobayashi

Energy-filtering transmission electron microscopy is applied to a single carbon nanotube in order to investigate quantitative property of elemental maps obtained by inelastically scattered electrons corresponding to the carbon K-edge. We find that the contrast differences due to 20 carbon atoms or to 6 graphene sheets are well observed in the carbon distribution image with a nanometer resolution.

**Keywords:** Elemental Map/ Electron Energy-Loss Spectroscopy/ TEM

Energy-selecting technique based on an electron energy-loss spectroscopy (EELS) in conventional transmission electron microscopy [1] provides energy-filtered high-resolution image and diffraction, and also elemental map, which promise quantitative analyses of specimens. In particular the elemental mapping makes it possible not only to visualize a two-dimensional distribution of a particular element, but also to count the number of atom existing in a specific region by analyzing the intensity of image quantitatively. In order to investigate the quantitative property of an elemental map, a thin specimen is needed because multiple scattering of electrons disturbs the intensity distribution. Here we report the usefulness of this technique for obtaining quantitative elemental distribution for the case of carbon nanotubes.

The structure of carbon nanotube is characterized by the inner and outer diameters of a tube and the number of graphene sheets [2]. Typical diameter of a tube is the order of nanometer which is thin enough to analyze the intensity of the elemental distribution image without any corrections on multiple scattering.

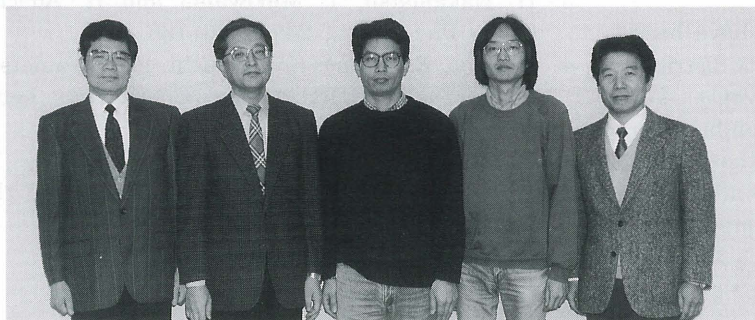
Since the structural parameters of each nanotube can be determined definitely from a high-resolution electron micrograph, the carbon distribution image observed from a well-defined nanotube is very suitable for examining the quantitative property of the elemental mapping. The investigations were performed using the 1MeV atomic resolution electron microscope (JEOL) [3] equipped with a Gatan imaging filter (GIF) [4].

High resolution lattice image and carbon distribution image of self-supported nanotubes were observed at a magnification of the microscope of 20,000x which corresponds to an effective magnification of 340,000x on the slow-scan CCD camera of the GIF. This means that the pixel size referred back to the objective plane is 0.07nm which allows us to observe the elastic image of the (002) lattice planes ( $d=0.34\text{nm}$ ) of graphite. This magnification is, therefore, enough to characterize the structure of each nanotube by imaging graphene layers. In the carbon distribution images, however, the intensities of 4x4 pixels were integrated into one effective pixel (binning mode) because of the small

## STATES AND STRUCTURES — Crystal Information Analysis —

### Scope of research

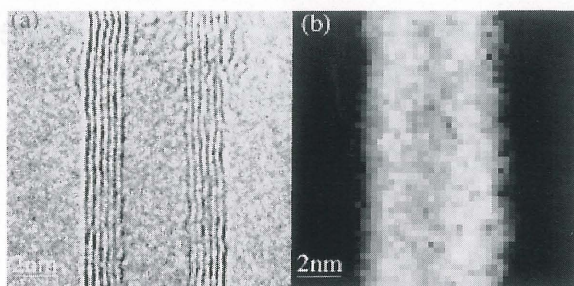
*Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of organic materials, and development in high resolution electron spectromicroscopy including electron energy-loss spectroscopy.*



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**Figure 1.** (a) High-resolution lattice image of a single nanotube and (b) corresponding carbon distribution image.

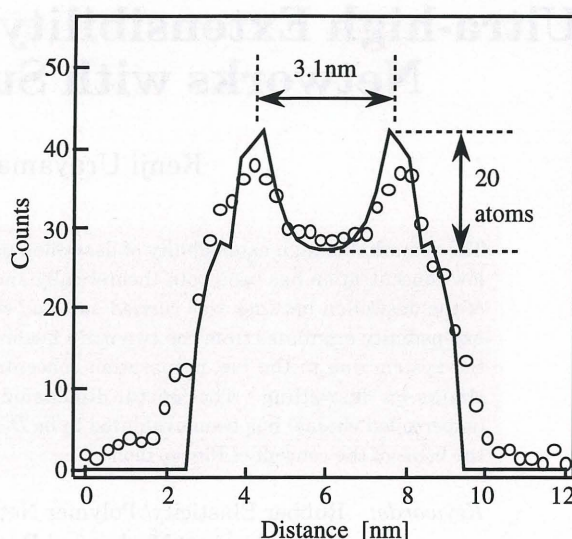
inelastic scattering cross-section of the carbon K-edge compared to that of elastic scattering, so that the effective pixel size became 0.28nm.

Typical high-resolution lattice image of a single nanotube and its carbon distribution image formed with electrons lost their energy by exciting the K-shell of carbon are shown in Figure 1a and 1b, respectively. The lattice image clearly indicate the 6 layered cylindrical structure. The outer and inner diameters of the tube are 6.5nm and 3.15nm, respectively. Figure 2 shows the intensity profile of carbon distribution image across the tube axis in which the intensities measured are plotted by the open circles. The intensity of the carbon profile increases from the vacuum to the inside of the tube, which indicates the increase of the number of carbon atom. The intensity maxima separated with a distance of 3.1nm are observed in the line profile. Here, we relate quantitatively such a characteristic carbon profile to the atomic distribution determined by the following procedure.

Within the thin film approximation, the image intensity at each pixel of the detector is proportional to the number of carbon atoms projected on each pixel of the detector. The proportional constant is related to the electron dosage irradiated on the specimen, the partial inelastic scattering cross-section of carbon K-edge and the conversion efficiency of the detector system. These values were determined: the electron dosage was measured to be  $1.25 \times 10^7$  electron/nm<sup>2</sup> and the inelastic scattering cross-section was calculated using the SIGMAK software [5] with the collection angle of 10mrad and the energy window of 30eV. Since the incident electron energy is 1MeV, relativistic correction for the inelastic cross-section was included in the present calculation. The conversion efficiency of the detector system is 0.3 in the present device. The number of carbon atom projected on each pixel of the detector can be simply estimated by assuming the 6 layered cylindrical structure observed in Figure 1a.

The agreement of the experimental and theoretical intensity profiles is quite satisfactory (Figure 2), which means the elemental distribution image is highly quantitative as long as a thin specimen is examined. The intensity maxima and minimum at the central region of the nanotube correspond to about 50 and 30 carbon atoms per pixel, respectively. Therefore, we conclude that the difference of 20 carbon atoms can be detected at nanometer scale with a good signal to noise ratio.

Similar observation and analysis have been performed on the conical tip region of a nanotube. The lattice image shows that the tip is made by progressive multilayer of curved graphene sheets [6].



**Figure 2.** Comparison between the experimental intensity profile of carbon distribution image and the calculated one.

In one case the numbers of layers are 5, 8 and 14 layers from the tip to inside of the tube. Since the tip has a conical symmetry about the cone axis, the number of carbon atoms is constant in the respective multilayer regions. Such the distribution of the carbon atoms was visualized by the elemental mapping. The intensity profile along the cone axis showed the stepwise intensity change from the tip to inside of the tube as expected from the increase of graphene layers. The differences of the step height in the line profile correspond to 6 and 12 graphene layers, respectively, because the electron beam travels through the upper and lower multilayers of the nanotube. Such differences of the graphene layers are equivalent to 18 and 36 carbon atoms per pixel, respectively. In this example, therefore, we can also detect the difference of about 20 carbon atoms.

Our observations [7] establish that the energy-filtering technique based on EELS is very powerful to analyze the elemental distribution quantitatively with a nanometer resolution. For the ultimate single atom analysis it should be necessary to irradiate much stronger electron beam than the present experiment. However, the nanotubes suffer structural distortion from intense electron irradiation, so that the observed detection limit is restricted by the stability of specimen to electron beam.

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# Ultra-high Extensibility of Deswollen Polysiloxane Networks with Supercoiled Structure

Kenji Urayama and Shinzo Kohjiya

The remarkable high extensibility of deswollen polysiloxane (PDMS) network crosslinked in solution with low concentration has been both theoretically and experimentally demonstrated. The uniaxial elongation of the deswollen network was carried out, and the elongation at break reached at ca. 1700%. This high extensibility originates from the two main factors: no or a negligible amount of trapped entanglements in the system due to the low preparation concentration; the reduction of end-to-end distance of network chains on deswelling. The fractal dimension ( $D$ ) of the contracted network chains on deswelling (supercoiled chains) has been evaluated to be  $D=2.5$  from the dependence of stress on elongation ratio on the basis of the concept of Pincus blob.

**Keywords:** Rubber Elasticity/ Polymer Network/ Supercoiling/ Deswelling/ Trapped Entanglement/ Mechanical Property/ Fractal Dimension

The elastic properties of the deswollen polymer networks, which are prepared by removing solvent from the network crosslinked in solution (deswelling), are still an unsettled subject in the physics of rubber elasticity [1]. The deswelling process is accompanied by the collapse of the network-chain conformation due to the volume decrease of material, which complicates the quantitative understanding of the elasticity of deswollen networks. The contraction of polymeric network chains on deswelling has often been called "supercoiling" [1]. The supercoiled chains are assumed to have the contracted conformation relative to the Gaussian chains, but the details on the conformation of supercoiled chains and the effects of supercoiling of network chains on the mechanical properties of deswollen networks are not well-known.

Another topic for the deswollen polymer networks

is that the deswollen networks prepared from the solution with low polymer concentration can exhibit the remarkable high extensibility in comparison with the conventional elastomers [2,3]. The upper limit of extensibility for the crosslinked rubber can be roughly evaluated by the following equation.

$$\lambda_{max} \approx bN_e / (bN_e^{1/2}) = N_e^{1/2} \quad (1)$$

Here,  $\lambda_{max}$  is the elongation at break, and  $b$  is the Kuhn segment length, and  $N_e$  is the number of Kuhn segment between the neighboring crosslinking points when the trapped entanglement points are treated similarly as the chemical crosslinks. The trapped entanglements are the physical crosslinking points created by the uncrossability of mutual network chains. Since the typical value of  $N_e$  in the polymer melt is 20~40,  $\lambda_{max}$  is limited to 4~6. This value of  $\lambda_{max}$  explains well the fact that  $\lambda_{max}$  for

## STATE AND STRUCTURES — Polymer Condensed States —

### Scope of research

*Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystals and polymer composites, mainly by electron microscopy and X-ray diffraction/scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution and in situ studies on structural formation/change in crystalline polymer solids.*



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conventional elastomers rarely exceeds 10. The restriction of  $\lambda_{max}$  mainly originates from the existence of the large amount of the trapped entanglement which acts similarly as the chemical crosslinks. Equation (1) means that the enhancement of  $\lambda_{max}$  needs the increase of  $N_e$ , namely, the decrease of the amount of trapped entanglement. To crosslink the polymer chains at the solution state is a simple method to increase  $N_e$ . The value of  $N_e$  increases with decreasing  $\phi_o$  as  $N_e \sim \phi_o^{-1}$  where  $\phi_o$  is the polymer volume fraction at the preparation state [4]. Furthermore, it should be noticed that the deswelling process causes the reduction of end-to-end distance ( $R$ ) of network chains at undeformed state due to the large volume change. If the crosslinking points move affinely on deswelling, the value of  $R$  at undeformed state ( $R_o = bN^{1/2}$ ) is reduced to  $R_o \phi_o^{1/3}$ . The value of  $\lambda_{max}$  for the deswollen networks prepared at  $\phi_o$  is evaluated as follows.

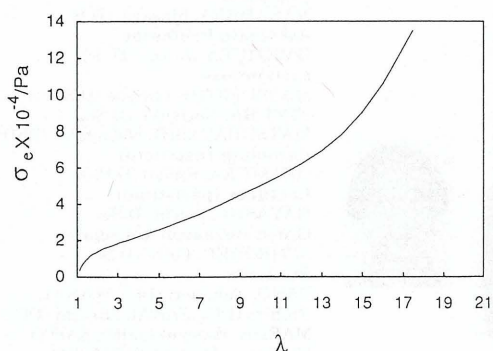
$$\lambda_{max} \approx bN_e \phi_o^{-1} / (bN_e^{1/2} \phi_o^{-1/2} \phi_o^{1/3}) = N_e^{1/2} \phi_o^{-5/6} \quad (2)$$

Equation (2) means the value of  $\lambda_{max}$  for the deswollen networks prepared at 10% solution reaches 30~40 which is ca. 7 times as large as that of the networks crosslinked at melt state.

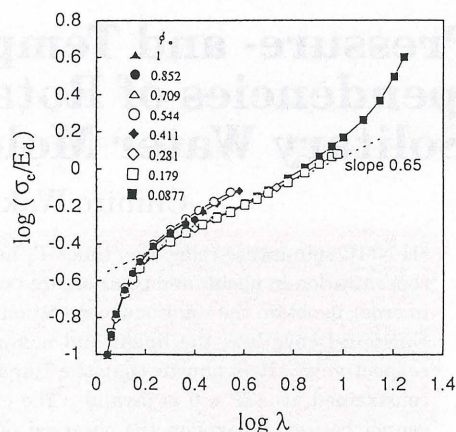
We have prepared the deswollen polymer networks by means of the endlinking reaction between vinyl-terminated polydimethylsiloxane (PDMS) and tetradimethylsiloxysilane in toluene. The value of  $\phi_o$  was varied from 0.0877 to 1. The weight average molecular weight of PDMS is 47000.

Figure 1 shows the stress ( $\sigma_e$ ) - elongation ( $\lambda$ ) curve for the deswollen PDMS network prepared at  $\phi_o = 0.0877$ . Here,  $\sigma_e$  is the stress per the cross-sectional area at undeformed state. As can be seen, the deswollen PDMS network with  $\phi_o = 0.0877$  shows a remarkable high extensibility reaching  $\lambda_{max} \approx 18$ . And we have confirmed that the deswollen network exhibits the almost complete elastic recovery. The theoretical value of  $\lambda_{max}$  for the deswollen PDMS network with  $\phi_o = 0.0877$  is evaluated to be  $\lambda_{max} = 20$  per the above discussion together with the consideration for the stiffness of PDMS chain. The experimental result ( $\lambda_{max} = 18$ ) is found to be close to the theoretical limit.

We indicate the double logarithmic plots of  $\sigma_e$  vs.



**Figure 1.** Stress-elongation curve of deswollen PDMS network prepared at ca. 9% solution.



**Figure 2.** Double logarithmic plots of stress vs. elongation for deswollen PDMS networks.

$\lambda$  for the deswollen networks in Figure 2. The stress is renormalized by  $E_d$  of each sample. Here,  $E_d$  is the initial Young's modulus. It is found that the stress-elongation relations of deswollen networks are divided into two groups: the networks prepared at  $\phi_o \leq 0.281$ , and those at  $\phi_o \geq 0.411$ . The overlapping of the curves suggests that the deswollen networks in each group have the common topological features. The major difference of the curves in each group is only in the extensibility. The dependence of  $\sigma_e$  on  $\lambda$  for the deswollen networks with  $\phi_o \leq 0.281$  is found to obey  $\sigma_e \sim \lambda^{0.65}$  in the region  $2.1 \leq \lambda \leq 5.5$ . We regard this region  $2.1 \leq \lambda \leq 5.5$  as the disentanglement process of the supercoiled structure, and estimate the fractal dimension ( $D$ ) of the supercoiled structure from the dependence of  $\sigma_e$  on  $\lambda$  on the basis of the treatment of the large deformation for a flexible polymer chain by Pincus [5]. According to the concept of Pincus blob, the stress-elongation relation in the elongational process of the polymer chain with  $D$  is described by the following equation [1,5].

$$\sigma_e \sim \lambda^{D-1} \quad (3)$$

The value of  $D$  for the supercoiled structure is evaluated to be 2.5 from this equation [3]. This fractal dimension ( $D=2.5$ ) is larger than  $D=2$  for the Gaussian chain, while that is smaller than  $D=3$  or 4 for the "polymer chain in an array of obstacles" (PCAO) model. The PCAO is one of the models describing the strongly collapsed conformation of polymer chains [6]. Our experimental result suggests that the supercoiled chain is contracted in comparison with the Gaussian one, while it is not collapsed as strongly as the PCAO models.

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# Pressure- and Temperature-Variable Viscosity Dependencies of Rotational Correlation Times for Solitary Water Molecules in Organic Solvents

Chihiro Wakai and Masaru Nakahara

$^2\text{H}$ -NMR spin-lattice relaxation times  $T_1$  have been measured for solitary water molecules ( $\text{D}_2\text{O}$ ) at a low concentration in apolar and polar organic solvents ( $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , and  $\text{CH}_3\text{CN}$ ) at  $30^\circ\text{C}$  at high pressures in order to obtain the rotational correlation times  $\tau_{2R}$ . We have tested the two forms of modified Stokes-Einstein-Debye law; the linear and nonlinear forms are  $\tau_{2R} = \tau_{2R}^0 + S(\eta/T)$  and  $\tau_{2R} = B(\eta/T)^\alpha$ , respectively. It is shown that the linear form is practically better, and that the nonlinear form constrained at  $\eta/T = 0$  is invalid. The extended-diffusion models based on isolated binary collisions cannot be used to explain the observed pressure effect because of the neglect of the attractive solute-solvent interactions.

**Keywords:** Rotational friction/ Hydrodynamic model/ High-pressure NMR

The rotational correlation time  $\tau_{2R}$  is often estimated in the framework of the Stokes-Einstein-Debye (SED) law based on the hydrodynamic model. As discussed previously [1, 2], the SED law is usually modified as follows. The linear form with an intercept is

$$\tau_{2R} = \tau_{2R}^0 + S(\eta/T), \quad (1)$$

and the nonlinear form without an intercept is

$$\tau_{2R} = B(\eta/T)^\alpha. \quad (2)$$

Here,  $h$  is the solvent viscosity,  $S$  and  $B$  are the constants, and  $\alpha$  is the fractional viscosity exponent. As seen from Fig. 1, Eq. (1) is obviously superior to Eq. (2). The data fit to Eq. (2) is not natural but merely forced to pass the zero value of  $\eta/T$ . The zero-point constraint makes the fit curve (broken line) concave upward with a fractional power. The intercept is significantly larger with a smaller slope in the pressure-variable experiment than in the temperature-variable experiment. The large positive

intercept in Eq. (1) gives rise to the fractional nature of the viscosity exponent in the fit to the form of Eq. (2).

Figure 2 illustrates the temperature- and pressure-variable density dependencies of  $\tau_{2R}$ . In the pressure-variable experiment, the dependencies are much larger than the prediction of the extended-diffusion model based on isolated two-body collisions. In the temperature-variable experiment, the  $\tau_{2R}$  vs  $\rho_N$  curve rises very sharply in any system. This is mainly due to the kinetic effect which may be represented by an exponential factor of the Arrhenius type.

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## INTERFACE SCIENCE — Solutions and Interfaces —

### Scope of research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biochemical interests are systematically studied by NMR under extreme conditions. Simple and complex solution systems are supercooled, overheated, and compressed to high pressures to shed light on microscopic factors which control rotational and translational motions of ions and molecules. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Crystallization of protein monolayers, advanced dispersion systems at liquid-liquid interfaces, and biomembranes are also investigated.



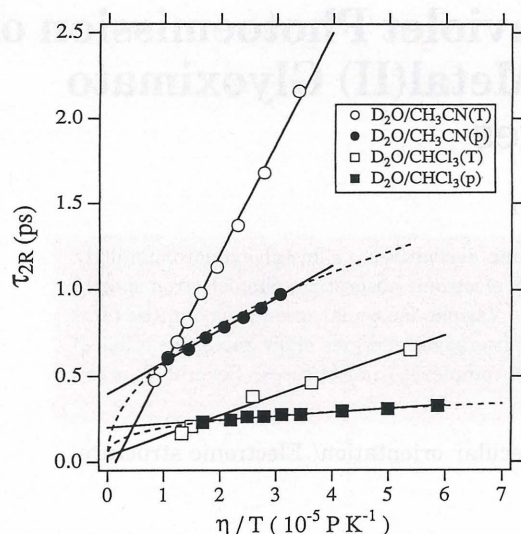
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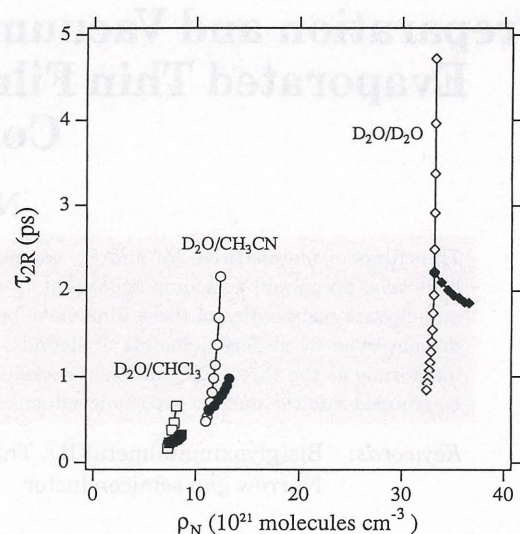
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**Figure 1.** Plots of the rotational correlation times for  $D_2O$  in  $CH_3CN$  and  $CHCl_3$  against solvent viscosity divided by temperature. Open and solid symbols are for temperature- and pressure-variable viscosity variations, respectively. Circles and squares denote  $D_2O/CH_3CN$  and  $D_2O/CHCl_3$  systems, respectively.



**Figure 2.** Plots of the rotational correlation times for  $D_2O$  in  $CH_3CN$ ,  $CHCl_3$ , and pure liquid against the number densities ( $\rho_N$ ) of the solvents for pressure- (solid symbols) and temperature-variable (open symbols) experiments.

## Quantitative Analysis of Uniaxial Molecular Orientation in Langmuir-Blodgett Films by Infrared Reflection Spectroscopy

Takeshi Hasegawa, Satoshi Takeda, Akira Kawaguchi, and Junzo Umemura

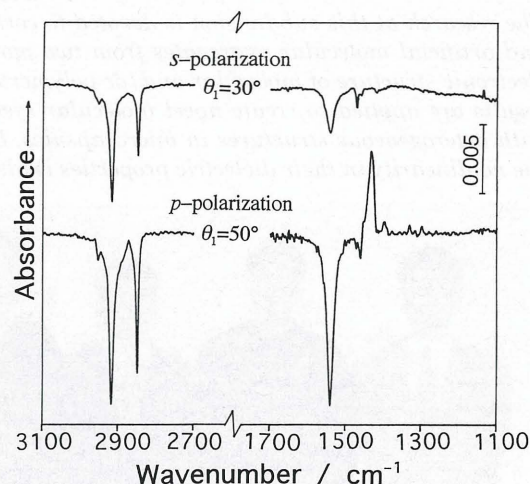
A new method for calculating infrared reflection-absorbances of multilayered LB films with a uniaxial anisotropy around the surface normal was developed, to analyze optical properties and molecular orientations in ultrathin films.

**Keywords:** Molecular orientation/ Langmuir-Blodgett films/ FT-IR external reflection spectra/ Uniaxial anisotropy

With this method, infrared external reflection spectra of a 9-monolayer Langmuir-Blodgett (LB) film of Cd stearate prepared on a GaAs substrate (Figure 1) were analyzed, and the tilting angle of the hydrocarbon chain was obtained as  $14^\circ$  from the surface normal, in fair agreement with that obtained by X-ray diffractometry. Reflection-absorption spectra of the same LB film on a silver-evaporated slide glass at various temperatures were also analyzed by the same method and the orientation angle of each molecular group was obtained, clarifying the process of disordering with the increase of temperature. Further, the dependence of the degree of disordering on the monolayer location in LB films were discussed in light of the isotope substitution experiment [1].

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**Figure 1.** FT-IR external reflection spectra of 9-monolayer LB film of Cd stearate on GaAs.



# Preparation and Vacuum-Ultraviolet Photoemission of Evaporated Thin Films of Metal(II) Glyoximate Complexes

Naoki Sato

Thin films of metal(II)(Ni, Pd and Pt) complexes of glyoxime derivatives, *i.e.*, bis(glyoximate)metal(II), have been prepared by vacuum deposition. X-ray diffraction, electronic absorption, photoelectron spectra and electric resistivities of these films have been measured. Various molecular orientations in the films are observed for different metals or ligands. The lowest absorption energies show the same order of magnitude as the threshold ionization energies from Ni to Pt complexes in most cases. Several films can be grouped into the narrow gap semiconductors.

**Keywords:** Bis(glyoximate)metal(II)/ Thin film/ Molecular orientation/ Electronic structure/ Narrow gap semiconductor

Most of planar molecular complexes of group ten metals coordinated by two molecules of glyoxime derivatives (Rgly),  $M(Rgly)_2$  ( $M = Ni, Pd$  and  $Pt$ ), stack in the manner that their  $d_{z^2}$  orbitals of  $d_8$  metal ions overlap with each other, so that their crystal structures are characterized by one-dimensional arrangements of metal ions in the direction perpendicular to the molecular plane. We have tried to prepare evaporated thin films of these molecules and to examine structures and properties of the obtained films, in particular, their valence electronic structures using ultraviolet photoemission measurements.

Materials studied in this work were group ten metal complexes of glyoxime derivatives as follows: dimethylglyoxime (dmg), diphenylglyoxime (dpg), diaminoglyoxime (dag), 1,2-cyclohexanedione dioxime or nioxime (niox), 1,2-benzoquinone dioxime (bqd), 1,2-acenaphthenequinone dioxime (anqd), 9,10-

phenanthrenequinone dioxime (paqd). These ligand molecules were synthesized and the metal complexes were prepared by mixing the hot water-alcohol solutions containing stoichiometric amounts of a metal salt ( $NiCl_2$ ,  $K_2PdCl_4$  or  $K_2PtCl_4$ ) and a ligand, respectively. The final products were purified by repeated recrystallization from *e.g.*, *N,N*-dimethylformamide or *o*-dichlorobenzene. Chemical composition of all materials used were confirmed by elemental analysis.

Thin film preparation of  $M(Rgly)_2$  ( $M = Ni, Pd, Pt$ ) was tried by vacuum deposition onto a quartz-glass or a polycrystalline copper substrate held at room or a regulated temperature using a low heat capacity evaporation source in vacuum where the pressure was about  $1.33 \times 10^{-4}$  Pa [1]. Thermal decomposition of most materials in the source was competed with their film deposition, especially at a deposition rate

## INTERFACE SCIENCE — Molecular Aggregates —

### Scope of research

*The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric behaviors. The electronic structure of molecular and/or polymeric thin films is studied in connection with the former, and its results are applied to create novel molecular systems with characteristic functions. The latter is concerned with heterogeneous structures in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.*



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no more than 0.2 nm/min. Only  $M(dag)_2$  did not give a film even at a rate much higher than 0.2 nm/s. The thicknesses of films obtained for the complexes of the other six kinds of ligands, monitored by a quartz oscillator, were ranged from 50 to 150 nm. X-ray diffraction profiles, electronic absorption spectra, ultra-violet photoemission spectra [2] and electric resistivities of the complex films were measured in most cases at room temperature to study characteristics of their structural and electronic properties.

Molecular orientations in the films have been examined to be dependent on the compound and/or deposition conditions, in particular, the substrate. For example, on a quartz-glass substrate, a  $Ni(bqd)_2$  film is amorphous, while  $Pd(bqd)_2$  and  $Pt(bqd)_2$  films are uniaxially oriented [3]. Further, a  $Pt(dmg)_2$  film is oriented with the molecular stacking axis parallel to a quartz-glass surface, whereas perpendicular to a graphite surface. The lowest electronic absorption energies, assigned to the electronic transitions from  $nd_{z^2}$  to  $(n+1)p_z$  levels for Pd and Pt complexes in most cases, show the same order of magnitude as their threshold ionization energies from Ni to Pt complexes

in most films. The  $Pt(bqd)_2$  film shows the lowest value of the transition energy 0.99 eV in all the compounds measured in this work. Its threshold ionization energy 4.96 eV is as small as the lowest values ca. 4.8 eV for  $Pt(niox)_2$  and  $Pd(anqd)_2$  films. Thus, these data as well as the results of electric resistivity measurements lead to a conclusion that several films above can be grouped into the narrow gap semiconductors of molecular origin.

This work has partially been carried out in cooperation with Profs. I. Shirotani (Muroan Inst. Tech.), M. Yamashita (Nagoya Univ.) and S. Kitagawa (Tokyo Metropol. Univ.). The author thanks K. Ono (Univ. Tokyo) for collaboration in part.

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## Electrical Properties of Peptaibol-induced Ion-channels in Bilayer Lipid Membranes

Koji Asami, Norihiro Koide and Akira Matsubara

Peptaibols are antibiotic peptides, some of which produce voltage dependent ion-channels in bilayer lipid membranes (BLM). In this report we describe the electrical properties of ion-channels formed in planar bilayer lipid membranes by trichocellin and template-assembled alamethicins.

**Keywords:** Single-channel recording/ Template-assembled synthetic peptide/ Trichocellin/ Alamethicin

Peptaibols are a family of antibiotic peptides that contain  $\alpha$ -aminoisobutyric acid residues and have an  $\alpha$ -aminoalcohol at the C-terminal. Alamethicin, an extensively studied peptaibol, forms voltage-dependent ion-channels in BLM. The electrical properties of the channels are interpreted in terms of a barrel-stave model, a bundle of parallel helices spanning BLM. Studies of the ion-channels formed by peptaibols, which is much simpler in structure than ion-channel proteins, would provide useful knowledge on the relationship between the ion-channel structure and function. In this study, we focus on the electrical properties of the ion-channels formed in planar BLMs by trichocellin and template-assembled alamethicins (called  $ALn$ -cyclo $2n$ ) that have been prepared by linking  $n$  alamethicin monomers to a cyclic pseudopeptide, cyclo(Lys-mAbz) $n$ .

Trichocellin formed ion-channels with several discrete conductance states corresponding different pore sizes. The low-conductance state channels showed nonlinear current-voltage curves, which may result from the interaction between ions and the pore wall.

All the channels observed with KCl solutions were slightly cation-selective. The order of ion selectivity among alkali metal cations was  $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$  with 3 M chloride salt solutions. The selectivity order is close to the mobility sequence for the ions in aqueous solution, suggesting that the channels behave as a water-filled pore and the ions pass through the channels in hydrated form.

For template-assembled peptides, it would be expected that one peptide molecule produces one ion-channel with a definite pore size and that the channel has a long open lifetime. All the tree  $ALn$ -cyclo $2n$  peptides ( $n=3-5$ ) formed long-lived channels. The unitary conductances of the  $AL3$ -cyclo $6$  ( $n=3$ ) and  $AL4$ -cyclo $8$  ( $n=4$ ) channels were in agreement with the lowest and the next lowest conductances of the alamethicin channel, respectively, whereas the  $AL5$ -cyclo $10$  channel had various conductance states. This finding may imply that the structural rigidity of the template peptides is one of the important factors in determining the ion-channel properties.



# Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan

Yoshiki Sohrin, Takuya Tateishi, Masakazu Matsui, Munetsugu Kawashima\* and Hiroshi Hasegawa†

Aquatic organisms metabolize arsenic, forming non-toxic arsenic-containing ribofuranosides and arsenobetaine from arsenate. The metabolism results in the occurrence of thermodynamically unstable arsenite and methylarsenicals in natural waters. We studied the seasonal variations of arsenical species in the mesotrophic northern and eutrophic southern basins of Lake Biwa in Japan. The total arsenic concentration in the euphotic zones remained constant in the northern basin, while it was increased by 2-4 times in the southern basin in summer. Despite the larger biomass, the percentage of methylarsenicals was lower in the southern basin. These results indicate that the eutrophication may alter the concentration and speciation of trace elements in the hydrosphere.

**Keywords:** Arsenate/ Arsenite/ Methylarsenicals/ Ferromanganese oxides/ Aquatic organisms

Lake Biwa is the largest lake in Japan and located in the center of Honshu (Fig. 1). The lake is a source of water supply for the fourteen million people living in the Kansai area and supports many kinds of aquatic organisms including more than 50 endemic species. The northern basin is located in a rural area and has a surface area of 616 km<sup>2</sup> and an average depth of 44 m. The southern basin is located in urban area and has a surface area of 58 km<sup>2</sup> and an average depth of 3.5 m. The waters in the northern basin flow into the southern basin and flow out through the Seta River. The residence time of water is estimated to be 5.5 y for the northern basin and 0.04 y for the southern basin. Nowadays the northern and southern basins are estimated as mesotrophic and eutrophic, respectively, because of human activity. The lake is an intriguing environment, since

one can observe a difference in the progression of eutrophication in the two originally identical basins.

Our observation was carried out from June, 1992 to February, 1995 mainly at stations N1 in the northern basin and S3 in the southern basin (1). We determined the concentrations of arsenate [As(V)], arsenite [As(III)], monomethylarsonic acid [MMAA(V)], monomethylarsonous acid [MMAA(III)], dimethylarsinic acid [DMAA(V)] and dimethylarsinous acid [DMAA(III)] in lake water (2). The concentrations of MMAA(III) and DMAA(III) were low (less than 0.3 nM), and therefore methylarsenicals were treated as MMAA(V+III) and DMAA(V+III). The total arsenic concentration was determined after the organoarsenicals were converted into As(V) by alkaline persulfate oxidation in a Teflon digestion bomb. This value agreed closely with  $\Sigma$  As, the sum of concentrations of As(V), As(III), DMAA(V+III) and MMAA(V+III). Therefore, these species comprise more than 95% of dissolved arsenicals in Lake Biwa.

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## INTERFACE SCIENCE — Separation Chemistry —

### Scope of research

*Our research activities are concerned in selective complex formation systems (molecular recognition). Major subjects of the research are followings: (1) Design and synthesis of the selective complex formation systems. Ligands (host molecules) that have novel functions in separation of metal ions and guest molecules are designed and synthesized. Their functions are analyzed basing on structures of the ligands and complexes. (2) Biogeochemistry of trace elements in the hydrosphere. Novel analytical methods for trace elements are developed. The behavior of trace elements in the hydrosphere is explored.*



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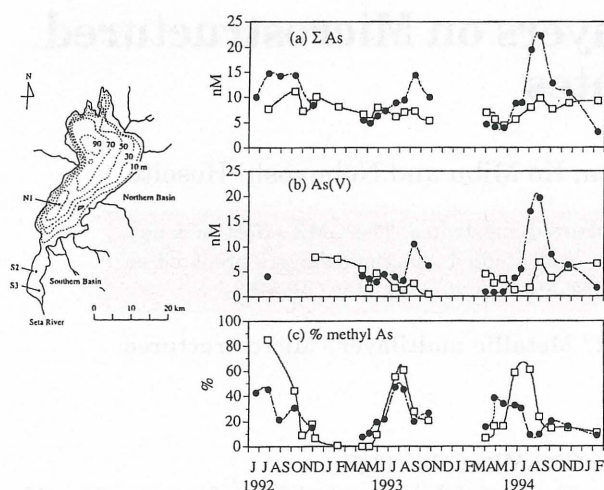


Figure 1. Location of sampling stations.

Figure 2. The seasonal variation of (a)  $\Sigma$  As, (b) As(V), (c) percentage of methylarsenicals, in the epilimnion. Open squares and filled circles show the data for the northern and southern basins, respectively.

Fig. 2 shows the seasonal change of arsenicals in the epilimnion. The  $\Sigma$  As in the southern basin was increased by 2-4 times in summer, while it was nearly constant in the northern basin. The enhancement was caused by the increase of As(V). Because there is no seasonal external source of As(V), it seems that the source is accumulated arsenicals in the sediments of the southern basin. Arsenicals are adsorbed onto ferro-manganese oxides in oxic lake water and settle to the bottom. When the ferromanganese oxides are reduced under anoxic condition, arsenicals are redissolved. Dissolved oxygen (DO) is normally never depleted in the hypolimnion in the shallow southern basin even in summer. S3 is located at a dredged area (0.25 km<sup>2</sup>, depth 13 m), where the water is stratified from June to September and DO is totally depleted in the hypolimnion. Thus, we could observe the anoxic process in a water column which normally occurs in the depth of the sediment. The vertical profiles of chemical species obtained at S3 on 30 August 1994 are shown in Fig. 3. DO was depleted below 8 m, and the concentrations of Mn, Fe, As(V) and As(III) increased toward the bottom. This indicates that ferromanganese oxides were reductively dissolved and released arsenicals. Phosphate, which is a chemical analogue of As(V), was concurrently released from the sediment.

The summer enhancement of  $\Sigma$ As in the epilimnion was also observed at other stations in the southern basin, such as S2 at the center of the basin. The maximum of  $\Sigma$ As was largest in 1994, when there was an unusually hot and dry summer. The water level of the lake fell to -123 cm on 15 September, which was the lowest level ever observed, and a large amount of algae withered around shallows of the southern basin. Since the large biomass in the basin promotes development of anoxic condition in the depth of the sediment, the release of arsenicals similar to that observed in the hypolimnion of S3 was apparently widespread in pore water of the sediment. Although most of arsenicals is adsorbed onto the

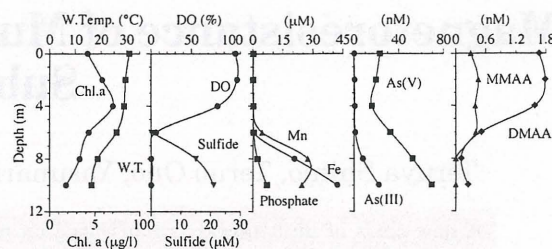


Figure 3. The vertical depth profiles of dissolved concentration of chemical species and water temperature at S3 on 30 August, 1994.

ferro-manganese oxides formed at the oxic surface of the sediment, some of them is supplied to the lake water. The supply was large in 1994, when local anoxic conditions were extensively developed in the surface sediments.

The change in speciation of arsenicals mainly occurred in the euphotic zone. As(V) was distributed uniformly through the water column in winter and its concentration decreased in the epilimnion in summer. As(III) increased during spring and fall blooms, while DMAA(V+III) became dominant in summer. The seasonal variation is probably a common feature of lakes and seas in the temperate zone. The speciation change is a result of the arsenic metabolism of phytoplankton and other aquatic organisms. The biomass in the southern basin is much larger than that in the northern basin as indicated by the concentration of chlorophyll a and transparency. It was reported that in 1993 the mean density of phytoplankton was 950 and 2500 cells/ml at the centers of the northern and southern basin, respectively. The southern basin contained more kinds of plankton species in addition to almost all dominant species observed in the northern basin. Although higher productivity is expected in the southern basin, the concentrations of As(III) and methylarsenicals produced through the arsenic metabolism were comparable to those in the northern basin. The percentage of methylarsenicals was low in the southern basin (Fig. 2). A culture experiment has revealed that uptake of As(V) by marine algae is inhibited competitively by phosphate at concentrations on the order of  $\mu$ M. While the phosphate was nearly depleted in the epilimnion in both the basins, the total budget of phosphorus was larger in the southern basin. The large load of phosphorus may have decreased the arsenic metabolism efficiency of phytoplankton in the southern basin. Another possibility is that degradation of organoarsenicals by bacteria may have been rapid in the southern basin because of its large population.

The eutrophication changed the concentration and speciation of the trace element in the water, and the change may further affect the ecosystem in the lake.

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# Magnetoresistance of Multilayers on Microstructured Substrates

Teruya Shinjo, Teruo Ono, Yasunari Sugita, Ko Mibu and Nobuyoshi Hosoiito

A new class of multilayers is fabricated on microstructured substrates. The GMR effect in a new geometry, (CAP, with current at an angle to the plane) was studied using multilayers prepared on micron-scale V-shaped groove structures. The measured CAP-MR is greater than the CIP-MR.

**Keywords:** Giant magnetoresistance / CPP-MR / Metallic multilayer / Microstructured substrate

Thin films are usually prepared on substrates with flat surfaces. Generally speaking, the sample quality can be high only if the surface is flat enough. On the other hand, a method to prepare thin films with new types of structural modifications is to use substrates with microstructured surfaces [1]. Multilayers deposited on microfabricated substrates may exhibit novel physical properties.

Since the discovery of giant magnetoresistance (GMR) in Fe/Cr multilayers, the interplay of magnetism and transport properties has attracted great attention [2]. The usual geometry of MR measurements for magnetic thin films and multilayers is with a current in the plane, which is abbreviated as CIP. In contrast, MR measurements with current perpendicular to the plane are called CPP. Generally, the MR ratio is expected to be larger in CPP geometry than in CIP, because conduction electrons meet more boundaries between magnetic and non-magnetic layers within their mean free paths. However, due to experimental difficulties, there are only a few reports

on CPP-MR studies [3-5].

The microfabrication technique for preparing a V-groove structure on a (100) Si surface using the anisotropic etching method has been well established [6]. A (100) oriented Si wafer, covered with a 1500 Å SiO<sub>2</sub> layer, was masked by photoresist and then a stripe pattern, 0.1 μm width and 1 μm separation, was printed by using electron beam lithography. By wet etching with KOH solution, V-shaped grooves were formed due to the different etching rates of (100) and (111) planes. Finally grooves are formed by the stable (111) planes and therefore the apex is the intersection of (111) planes, having the angle of 54.7°. The formation of microgrooves was confirmed by SEM.

On the V-groove microstructured substrates, a non-coupled type Co/Cu/NiFe/Cu multilayer was deposited. Due to the difference of coercive forces, the magnetizations of two components, Co and NiFe, are oriented antiparallel in the process of field sweeping and then the resistivity is greatly enhanced. As was

## SOLID STATE CHEMISTRY -Artificial Lattice Alloys-

### Scope of research

*By using vacuum deposition method, artificial multilayers have been prepared by combining various metallic elements. The recent major subject is the giant magnetoresistance (MR) in magnetic / non-magnetic multilayers. Non-coupled type MR multilayers including two magnetic components are found to have high sensitivities in low fields. Fundamental magnetic properties of large MR multilayers have been studied by applying Mössbauer spectroscopy, using Fe-57, Sn-119, Eu-151 and Au-197 as microprobes and by neutron diffraction. Novel magnetic and MR properties of multilayers prepared on microstructured substrate have been investigated*



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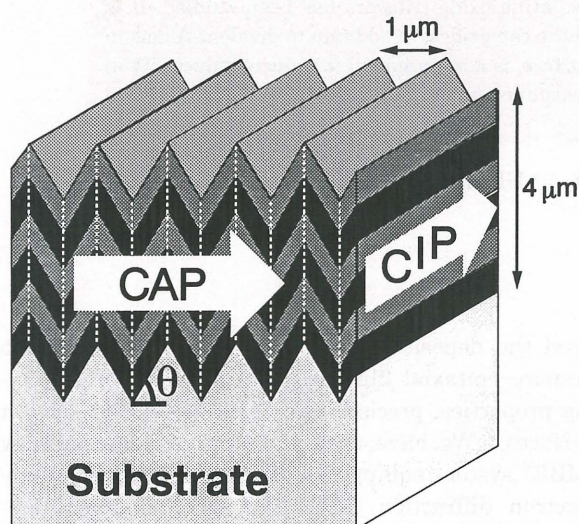
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reported already, such non-coupled multilayers have several definite merits for the study of GMR. A fairly large MR change can be induced by a small magnetic field, which is advantageous also for technical applications. Moreover, antiparallel magnetic alignment is realized at any spacer thickness as far as the inter-layer coupling is negligible and therefore the spacer layer thickness dependence of MR is easily studied.

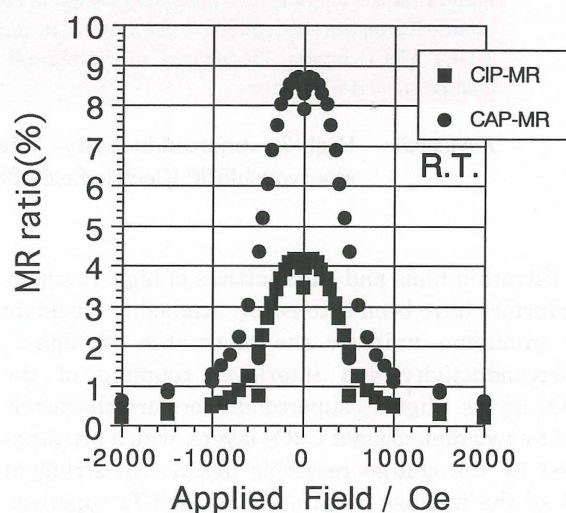


**Figure 1.** Schematic illustration of a multilayer prepared on a microstructured substrate. Current direction is indicated by arrow.

By depositing in the normal direction to the original (100) plane, multilayers with the structure as Figure 1 were prepared. The total thickness of deposited multilayers was  $4 \mu\text{m}$ . When the width of groove is  $1 \mu\text{m}$ , the height of groove should be  $0.7 \mu\text{m}$ , which is much smaller than the total multilayer thickness. Therefore, in the argument of transport phenomena, wrinkled parts of multilayers with triangular shape may be essentially neglected. If we measure the resistance with current perpendicular to the grooves in the plane of original (100) Si, the average current direction has an angle of  $54.7^\circ$  to the multilayer planes, and MR in a geometry with an angle to the plane (CAP) is studied. On the other hand, we can measure CIP-MR with the current parallel to the grooves. Figure 2 shows the results of magnetoresistance measurements at room temperature for the sample  $[\text{Co}(12\text{\AA})/\text{Cu}(116\text{\AA})/\text{NiFe}(12\text{\AA})/\text{Cu}(116\text{\AA})]_{167}$ . The result with the current parallel to the grooves and with the current perpendicular to the grooves is indicated by squares and circles, respectively. Magnetic field was applied parallel to the grooves in multilayer plane. The measured CAP-MR was greater than the CIP-MR. Moreover we can estimate

the CPP-MR value from observed CIP-MR and CAP-MR values by using the relation between CIP, CPP and CAP geometry which has been proposed by Levy et al [7].

Microstructured substrates are also useful to fabricate microwires. By depositing magnetic substance from a tilted direction onto a surface with  $0.5 \mu\text{m}$  groove, magnetic wires with  $0.3 \mu\text{m}$  width were obtained. These wires were afforded an uniaxial



**Figure 2.** MR curves at R.T. with the current parallel to the grooves (square) and with the current perpendicular to the grooves (circle). Magnetic field was applied parallel to the grooves in multilayer planes.

anisotropy due to the wire shape and the magnetic domain motions were studied from resistance measurements. Magnetic behaviors of multilayer wires are under investigation.

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# Superconductivity and Electric Field Effects in Ultrathin $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Films

Yoshichika Bando and Takahito Terashima

Effect of adjacent insulating cap oxide layers on superconductivity of one unit cell thick (1-UCT)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) layers in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ /YBCO/insulating oxide trilayers has been studied. It is found that the small lattice mismatch between YBCO and the cap oxides, in addition to divalent A ions in atomic AO layers subsequent to the  $\text{CuO}_{1-\delta}$  terminated surface, is a requirement for superconductivity in 1-UCT YBCO layers. The change in the normal state resistance is well explained by the field-induced change of carrier density.

**Keywords:** High- $T_c$  superconductivity /  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  / Ultrathin film / One-unit-cell / Charge reservoir block / Electric field effect

Ultrathin films and superlattices of high- $T_c$  superconductors have been extensively studied to elucidate the minimum unit for the occurrence of high- $T_c$  superconductivity and interlayer coupling of the  $\text{CuO}_2$  layers. High- $T_c$  superconductors are characterized by two dimensional  $\text{CuO}_2$  layers, which are separated by the charge reservoir blocks. A stringent test of the intrinsic nature of the high- $T_c$  superconductors characterized by layered structures can be obtained from transport measurements on one unit cell thick (1-UCT) layer of the superconductor. The smaller carrier density of high- $T_c$  superconductor than that in metal superconductor enables the change of carrier density by applying electric fields. The ultrathin films are expected to exhibit remarkable field effects in  $T_c$  and other properties.

In the preparation of such ultrathin layers, we

need the deposition technique which enables us to prepare epitaxial films with excellent superconducting properties, precise layer thicknesses and smooth surfaces. We have used a molecular beam epitaxy (MBE) system equipped with reflection high energy electron diffraction (RHEED), which enables real-time, *in situ* layer thickness monitoring by specular beam intensity oscillations [1].

We have found that superconductivity can occur at finite temperatures in the single layer of 1-UCT  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) sandwiched between nonsuperconducting  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (PrBCO) layers [2] and the minimum unit needed for the occurrence of superconductivity is the  $\text{CuO}_2$  bilayer sandwiched between the charge reservoir blocks, as shown in Fig. 1(a) [3]. It has been reported that the terminating surface of

## SOLID STATE CHEMISTRY — Artificial Lattice Compounds —

### Scope of research

*Syntheses of oxide thin films by reactive evaporation and ceramics by solid state reaction and their characterizations are studied. The main subjects are: preparation and characterization of ultrathin films of high- $T_c$  superconductors: investigation of growth mechanism of thin films by in situ reflection high-energy electron diffraction: phase diagram of  $\text{Bi}_2\text{O}_3$ - $\text{SrO}$ - $\text{CaO}$ - $\text{CuO}$  system: growth and characterization of single crystals of  $\text{Bi}$ - $\text{Sr}$ - $\text{Cu}$ - $\text{O}$  system: preparation and observation of dielectric properties of ferroelectric thin films: preparation and characterization of metallic and ferromagnetic  $\text{SrRuO}_3$  thin films: scanning tunneling microscope observation of surface structures and electronic states of metallic oxide thin films*



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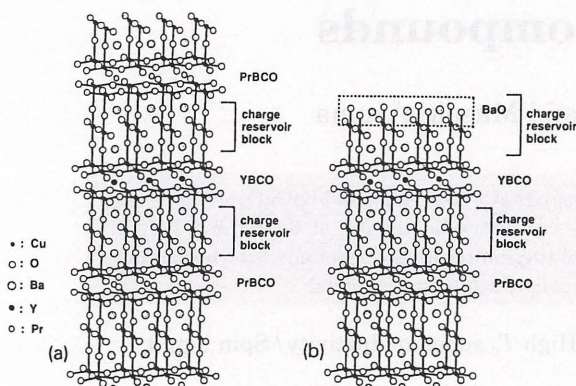
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**Figure 1.** Structures of trilayers of (a) PrBCO/1-UCT YBCO/1-UCT PrBCO and (b) PrBCO/1-UCT YBCO/BaO. Note that the  $\text{CuO}_2$  bilayer interposing an Y layer is sandwiched between the charge reservoir blocks and the terminating layers of growing YBCO and PrBCO are the  $\text{CuO}_{1-\delta}$  layer.

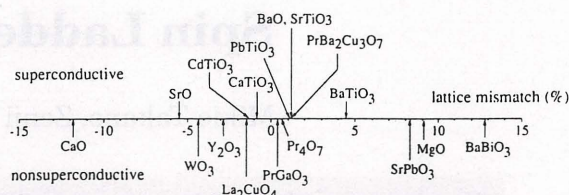
the YBCO layer grown by MBE is the  $\text{CuO}_{1-\delta}$  layer. As a result, the 1-UCT YBCO layer on the buffer PrBCO layer needs an addition of the BaO layer for the completion of the charge reservoir block, as shown in Fig. 1(b). It is found that the capping of the 1-UCT YBCO layer with BaO makes the 1-UCT layer superconducting.

In place of BaO layers, the effects of other alkaline-earth metal oxide "AO" caps on the superconductivity of the samples have been examined. The experimental results are summarized as a function of lattice mismatch value in Fig. 2. We can conclude that divalent metal ions in AO layer adjacent to the  $\text{CuO}_{1-\delta}$  layer, in systems with mismatch values ( $<6\%$ ) exhibit superconductivity in PrBCO/1-UCT YBCO/cap oxide trilayers.

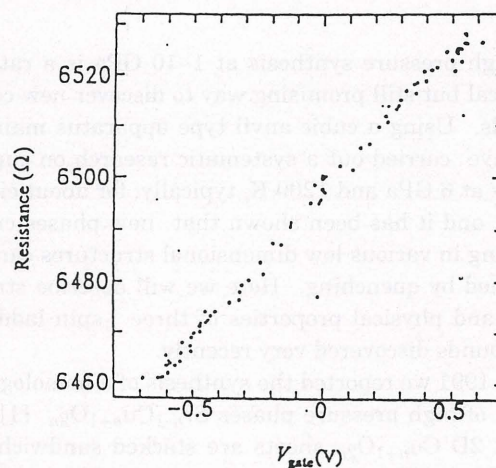
We have studied electric field effects in ultra-thin YBCO films using heterostructures of  $\text{Ag}/\text{BaTiO}_3(200\text{nm})/\text{SrTiO}_3(1.5\text{nm})/\text{YBCO}/\text{SrTiO}_3(\text{substrate})$ [4]. Gate voltage,  $V_{\text{gate}}$ , dependence for 2-UCT YBCO at 72.8K is shown in Fig.3. The application of negative voltage to the Ag electrode, i.e. the YBCO layer is positively charged, lowers the resistance of YBCO layer linearly in  $V_{\text{gate}}$ , while a positive  $V_{\text{gate}}$  having the opposite effect. The field induced change of the resistance  $\Delta R/R$  is 0.5% for the applied field of 0.5V.

Observed  $\Delta R/R$  in the normal state can be explained by the field induced carriers ( $\Delta N$ ). In the present experiment, field induced charge  $\Delta N$  in the areal density is evaluated as follows.

$$\Delta N = \Delta Q/e, \Delta Q = CV_{\text{gate}}/S, N = nd,$$



**Figure 2.** Effect of cap oxides on superconductivity in 1-UCT YBCO as a function of value of lattice mismatch to YBCO.



**Figure 3.** Gate voltage,  $V_{\text{gate}}$ , dependence of resistance for 2-UCT YBCO at 72.8K.

where  $S$  is area of electrode,  $N$  is total carrier of YBCO layer,  $d$  is the thickness of YBCO layer and  $n$  is carrier density of bulk YBCO.  $\Delta N/N$  is evaluated to be 0.55% by using the values of  $n = 5 \times 10^{21}(\text{cm}^{-3})$ ,  $C = 500(\text{nF})$  and  $S = 2.2 \times 10^{-1}(\text{cm}^2)$ . The observed  $\Delta R/R$  is in good agreement with the change of the carrier density,  $\Delta N/N$ .

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# Spin Ladder Compounds

Mikio Takano, Zenji Hiroi and Masaki Azuma

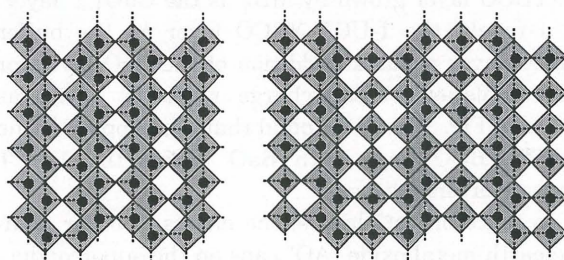
Three kinds of cupric spin ladder compounds,  $\text{SrCu}_2\text{O}_3$  (2-leg),  $\text{Sr}_2\text{Cu}_3\text{O}_5$  (3-leg), and  $\text{LaCuO}_{2.5}$  (2-leg), have been discovered in the course of studies of high pressure chemistry carried out at 6 GPa and 1200 K, typically. Structures, electrical and magnetic properties of these intriguing compounds, which exemplify the initial stage of the transition from one to two dimensionality, will be summarized.

**Keywords:** High pressure synthesis / Spin ladder / High  $T_c$  superconductivity / Spin liquid

High pressure synthesis at 1–10 GPa is a rather classical but still promising way to discover new compounds. Using a cubic anvil type apparatus mainly, we have carried out a systematic research on cupric oxides at 6 GPa and 1200 K, typically, for about eight years, and it has been shown that new phases crystallizing in various low dimensional structures can be obtained by quenching. Here we will describe structural and physical properties of three spin ladder compounds discovered very recently.

In 1991 we reported the synthesis of a homologous series of high pressure phases  $\text{Sr}_{n-1}\text{Cu}_{n+1}\text{O}_{2n}$  [1], in which 2D  $\text{Cu}_{n+1}\text{O}_{2n}$  sheets are stacked sandwiching  $\text{Sr}^{2+}$  ions in-between. As can be seen in Fig. 1 where the  $\text{Cu}_2\text{O}_3$  ( $n=3$ ) and  $\text{Cu}_3\text{O}_5$  ( $n=5$ ) sheets are illustrated, the  $\text{Cu}_{n+1}\text{O}_{2n}$  sheets are made of ladders with a  $n$ -dependent width: The longitudinal Cu–O–Cu chains are compared to the legs of a ladder and the lateral Cu–O–Cu bonds to the rungs. The leg number is equal to  $(n+1)/2$ . It is noteworthy that neighboring ladders are phase-shifted from each other and that the phase shift causes spin frustration between the

neighboring ladders. The  $\text{Cu}_{n+1}\text{O}_{2n}$  sheets can thus be considered as being made of tightly bound but magnetically separated  $(n+1)/2$ -leg ladders. For these compounds a dramatic change of electronic properties with leg number was predicted by Rice *et al.* in 1993 [2]: Ladders with an even number of legs have purely short range magnetic correlation and a finite energy

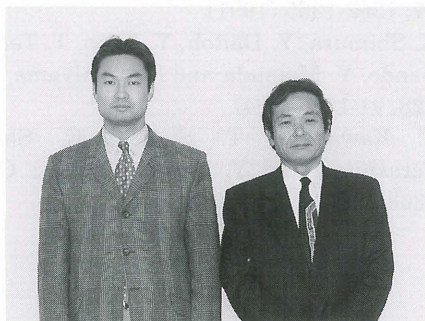


**Figure 1.** Schematic drawings of the  $\text{Cu}_2\text{O}_3$  sheet of  $\text{SrCu}_2\text{O}_3$  (left) and the  $\text{Cu}_3\text{O}_5$  sheet of  $\text{Sr}_2\text{Cu}_3\text{O}_5$  (right). The filled circles are  $\text{Cu}^{2+}$  ions, and  $\text{O}^{2-}$  ions exist at the corners of the gray squares. Cu ions interact antiferromagnetically with each other within each ladder as shown with dashed lines.

## SOLID STATE CHEMISTRY — Multicomponent Materials —

### Scope of Research

Novel inorganic materials that have new, useful or exotic features such as superconductivity, ferromagnetism and quantum spin ground state are synthesized by novel methods. Particularly the search for spin ladder materials is intensively conducted by means of a high pressure synthesis at 3–8 GPa, where materials of high density unavailable under ambient pressure can be obtained.



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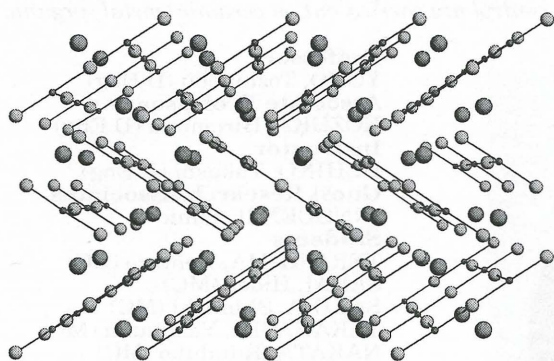
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gap to all magnetic excitations, while odd-leg ladders are gapless as a single chain is. The magnitude of the gap ( $\Delta$ ) is equal to  $J/2$  for an isotropic 2-leg ladder. And it has been predicted that holes doped in even-leg ladders will pair and possibly superconduct. For further details the readers are referred to a nice and compact review by Dagotto and Rice [3].

The electronic properties have been studied experimentally by means of SQUID magnetometry [4], NMR [5],  $\mu$ SR [6], and also inelastic neutron scattering [7]. All these showed quite consistently that the 2-leg ladder system assumes the so-called singlet spin liquid state, in which a Cu ion is coupled with the counter Cu ion on the same rung mainly. The magnitude of the spin gap was estimated to be 420 K from the temperature dependence of magnetic susceptibility [4], and the more recent direct determination using inelastic neutron scattering indicated a value of 410 K [7]. In marked contrast with the 2-leg ladder system that retains the unique coherent singlet ground state down to at least 20 mK, the 3-leg ladder compound becomes magnetically ordered at rather high temperatures [6]. Thus,  $\text{SrCu}_2\text{O}_3$  and  $\text{Sr}_2\text{Cu}_3\text{O}_5$ , which crystallize in essentially the same structures except for the leg number, have proved to show quite different magnetic properties. However, it has not been possible to test the possibility of high- $T_c$  superconductivity in the 2-leg ladder compound, because the solubilities at the Sr site of aliovalent cations like  $\text{Na}^+$  for hole-doping and  $\text{La}^{3+}$  for electron-doping proved to be low.

More recently, another 2-leg ladder compound  $\text{LaCuO}_{2.5}$  was found in the La-Cu-O system treated at 6 GPa and 1173 K [8]. There are, however, important differences between this compound and  $\text{SrCu}_2\text{O}_3$  concerning the anion coordination and the arrangement of ladders. In  $\text{LaCuO}_{2.5}$  the Cu ions are all five-fold coordinated, not four-fold coordinated as in  $\text{SrCu}_2\text{O}_3$ , and the ladders are divided into two groups which make an angle of  $68.5^\circ$  to each other, not all the ladders being parallel to each other as in  $\text{SrCu}_2\text{O}_3$ . The Cu-O distances in the inter-ladder Cu-O-Cu bond are 1.941 Å and 2.285 Å and the bond



**Figure 2.** Crystal structure of  $\text{LaCuO}_{2.5}$ . Small circle:  $\text{Cu}^{2+}$  ions, middle circle:  $\text{O}^{2-}$  ion and large circles:  $\text{La}^{3+}$  ions.

angle is  $152.2^\circ$ . Weak inter-ladder interactions would be mediated by this bond. The investigation of the electronic properties is in a preliminary stage. For example, susceptibility data seem to be inconsistent with NMR measurements. Theoretical fitting to the susceptibility data goes very well down to 5 K, from which the spin gap  $\Delta$  was estimated to be 474 K [8]. This value is comparable with that for  $\text{SrCu}_2\text{O}_3$ , 420 K. However, as will be reported soon, the temperature dependences of  $T_1$  and the NMR spectral intensity have revealed a rapid growth of spin-spin correlations which suggests the occurrence of a magnetic ordering at  $\sim 120$  K [9]. The ordering was confirmed by a more recent mSR measurement. This is quite inconsistent with the spin liquid picture suggested from the susceptibility data, in contrast to the case of  $\text{SrCu}_2\text{O}_3$  where the picture was supported by all the measurements quite consistently. Various additional measurements including elastic and inelastic neutron scatterings are in progress. In contrast to the case of  $\text{SrCu}_2\text{O}_3$  again, chemical substitution for the purpose of hole-doping can fortunately be done up to  $x = 0.2$  for  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_{2.5}$ . Resistivity at 300 K drops quickly from  $\sim 10^4 \Omega \text{ cm}$  for  $x = 0$  to  $\sim 10^{-2} \Omega \text{ cm}$  for  $x = 0.15$  and  $< 10^{-3} \Omega \text{ cm}$  for  $x = 0.2$ . There is, unfortunately, no sign of superconductivity down to 1.5 K anyway. The interpretation of these results might be complex in nature because of the effects of inter-ladder interactions [10] and random potentials caused by the aliovalent  $\text{Sr}^{2+}$ -for- $\text{La}^{3+}$  substitution.

The final conclusion to be drawn here is quite simple. Both physics and chemistry of spin ladder compounds are quite new. The researches summarized here are nothing but the first steps on the ladder [11]. We believe that there would be various interesting findings in the future in this new research field.

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## Sol-Gel-Derived Oxide Thin Films Containing Metal Nanoparticles - Control and Application of Surface Plasma Resonance

Hiromitsu Kozuka, Tadanori Hashimoto, Takashi Uchino and Toshinobu Yoko

SiO<sub>2</sub> coating films containing Au nanoparticles were prepared by the sol-gel method. The size and shape of the dispersed Au particles, which determine the characteristics of the surface plasma resonance (SPR), could be varied in a wide range; the size could be varied from 4 to 40 nm, and the shape was spherical or elongated depending on the preparation conditions. Elongated Au nanoparticles of aspect ratios of 2 - 4 could be precipitated and aligned along the microscopically oriented pseudoboehmite particles, suggesting the possible production of the films with anisotropic SPR. TiO<sub>2</sub> film electrodes containing dispersed Au or Ag nanoparticles were prepared by the sol-gel method. Anodic photocurrents were observed in the visible region, resulting from the SPR-enhanced excitation of electrons from the surface states.

**Keywords:** Nanocomposites/ Coating films/ Sol-gel method/ Inorganic photonic materials/ Photoelectrodes

Nanocomposites composed of ultrafine metal particles and oxide matrices are now attracting much attention as advanced photonic materials. Surface plasma resonance (SPR) of metal particles, which enhances the oscillating electric field inside and outside nearby the particles, is the source of optical effects such as enhanced fluorescence and Raman scattering (SERS) of molecules, and enhanced optical third order nonlinearity. What is demanded for preparing materials of SPR-induced optical functions are to control the size and shape of the metal particles and to incorporate metal particles in high volume fraction; the former determines the wavelength of SPR and the latter provides intense SPR. Another

challenging task is to align elongated metal particles in the matrices. Aligned, elongated metal particles exhibit anisotropic SPR, i.e., SPR that depends on the direction of oscillating electric field. Such materials with aligned texture can be used as polarizers in optical isolators.

For preparing composite materials containing metal nanoparticles in high volume concentration, the sol-gel method has many advantages, because undesired segregation of large metal particles, which easily occurs in solutions and glass melts, can be avoided in mesoporous gel matrices. In addition, the size and shape of the metal particles can be controlled through controlling the gel pore structure and

### SOLID STATE CHEMISTRY — Amorphous Materials —

#### Scope of research

*Inorganic amorphous materials with various functions are the targets of research in this laboratory. (1) To obtain a clear view of "what is glass" and the bases for designing functional glasses, we investigate the structure of glasses using X-ray and neutron diffraction analysis, high resolution MAS-NMR, and ab initio MO calculation. (2) To develop materials of high optical nonlinearity, we search heavy metal oxide-based glasses and transition metal oxide thin films, and evaluate the nonlinear optical properties by THG and Z-scan methods. (3) Using sol-gel method, synthesis and microstructure control are carried out on ceramic/metal/organic dye composite thin films.*



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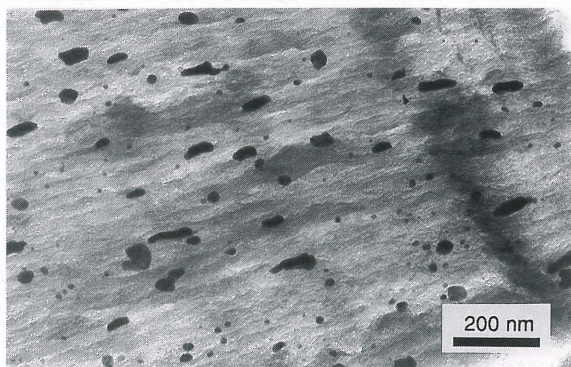
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the gel matrix properties.

SiO<sub>2</sub> coating films containing Au nanoparticles of 1 - 3 % in volume fraction were prepared from hydrolyzed Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> solutions containing HAuCl<sub>4</sub>·4H<sub>2</sub>O. The size of the Au particles could be varied from 4 to 40 nm, and the shape was spherical or elongated depending on the preparation conditions such as the sol aging time and the amount of H<sub>2</sub>O for Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> hydrolysis. Elongated Au nanoparticles could be precipitated in pseudoboehmite films and aligned along the microscopically oriented fibrous pseudoboehmite particles. TEM observation of the coating films revealed precipitation of aligned, elongated Au nanoparticles of aspect ratios of 2 - 4 (Fig. 1). The optical absorption due to SPR of Au particles, however, did not show any dependence on the direction of polarization, suggesting that the elongated Au particles are aligned only in a microscopic region. In order to achieve the macroscopically aligned texture, the dispersion state of the pseudoboehmite sol particles and the flow characteristics of the sol should be much more carefully controlled.

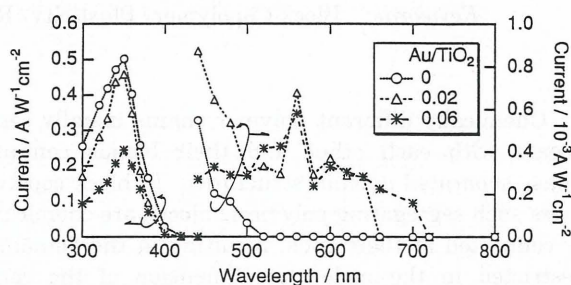


**Figure 1.** The TEM picture of a gel-derived pseudoboehmite coating film containing aligned, elongated Au nanoparticles.

Introduction of metal nanoparticles in photoelectrodes for solar cells is a possible innovative application of SPR. TiO<sub>2</sub> is believed to be one of the promising candidates for photoanode materials that split water due to its high chemical and photoelectrochemical durability. However, TiO<sub>2</sub> has low solar energy conversion efficiencies due to its large bandgap. Widely studied dye-sensitization extends the TiO<sub>2</sub> photoresponse to the visible region. In practice, however, the sensitizing quantum yield tends to be quite low, which is believed to be due to a fast back-reaction of the injected electrons. Enhancement of photochemical process of the sensitizers by SPR would be a possible way to increase the dye-sensitized quantum efficiency.

Firstly, the effect of Au and Ag nanoparticles on the photoelectrochemical properties of TiO<sub>2</sub> electrodes was investigated. TiO<sub>2</sub> film electrodes of 0.4

μm in thickness with a thin TiO<sub>2</sub> overlayer containing dispersed Au or Ag nanoparticles of 6 - 20 nm in size and 0.3 - 3 % in volume fraction were prepared by the sol-gel method. Anodic photocurrents were observed in the visible region for these electrodes (Fig. 2), which was thought to result from the SPR-enhanced excitation of electrons from the surface states. The introduction of larger amounts of the metal particles, however, reduced the anodic photocurrent in the UV region, resulting from the retardation of the electron transfer at the metal/TiO<sub>2</sub> Schottky barrier and by the TiO<sub>2</sub> band edge fluctua-



**Figure 2.** The action spectra of the TiO<sub>2</sub> film electrodes containing Au nanoparticles measured in a three electrodes system at a bias potential of 1 V vs. SCE.

tion.

Secondly, the effects of the incorporation of Au and Ag nanoparticles on the photoanodic properties were studied for rose bengal-deposited TiO<sub>2</sub> film electrodes. The dye-induced visible region photoresponse decreased with increasing Ag content, while the UV photoresponse increased. On the other hand, the dye-induced visible region photoresponse decreased to a less extent by incorporating Au particles, accompanied with the decrease in the UV photoresponse. Selection of metals, dyes and bias potentials and control of the separation between the metal particles and dye molecules would possibly improve the SPR-enhanced dye-sensitization.

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# Rheology of Diblock Copolymer Systems

Kunihiro Osaki, Hiroshi Watanabe, Tadashi Inoue, and Tomohiro Sato

AB diblock copolymers exhibit various microdomain structures and thus offer a rich field of rheology. In a low molecular weight, B-selective solvent, the AB diblock copolymers form regular lattices of micelles with A cores and B corona and exhibit plasticity. On the other hand, in polymeric B-selective solvents, homo-B chains, the copolymer micelles are randomly dispersed and viscoelastic relaxation prevails. Those AB/B blends exhibit fast and slow relaxation processes. The fast process is attributed to relaxation of individual corona B blocks tethered on the A cores, while the slow process is related to diffusion of the micelles.

**Keywords:** Block Copolymer / Plasticity / Relaxation / Entanglement / Tube Model / Diffusion

Chemically different polymer chains usually segregate with each other and their blends contain phase-separated domain structures. In block copolymers such segregating polymeric blocks are chemically connected at their ends, resulting in the domains restricted in the molecular dimension of the constituent blocks. This structure, called a microdomain structure, changes with the molecular weights and composition of the blocks as well as with the copolymer concentration (in the cases of solutions and blends). Various properties of the copolymer systems are strongly influenced by such microdomain structures. For styrene (S)-isoprene (I) and S-butadiene (B) diblock copolymers, we have found that their solutions exhibit unique rheological features that change with the nature of the solvents [1-4]. These features are summarized below in relation to the domain structures in the solutions.

In an I-selective, low molecular weight solvent, n-

tetradecane (C14), SB and SI diblock copolymers form micelles with precipitated S cores and solvated B and/or I corona. When the copolymer concentration is above a critical concentration for micelle overlapping, the micelles exhibit anomalous rheology that is characterized with highly nonlinear stress ( $\sigma$ ) - strain ( $\gamma$ ) patterns observed in dynamic tests using slowly oscillating strain. As an example, Figure 1 shows typical patterns found for a SB/C14 solution against small and large amplitude ( $\gamma_0$ ) strain [1,2].

In Figure 1, a rectilinear pattern indicating a proportionality between  $\sigma$  and  $\gamma$  is observed for small  $\gamma_0$  while a distorted, lozenge-shaped pattern is seen for large  $\gamma_0$ . These patterns characterize plasticity of the system: The proportionality between  $\sigma$  and  $\gamma$  indicates elastic behavior of the solution before yielding, and the lozenge-shaped pattern corresponds to elastic deformation and successive plastic flow repeated twice (in the opposite direction) during one

## FUNDAMENTAL MATERIAL PROPERTIES — Molecular Rheology —

### Scope of research

*The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.*



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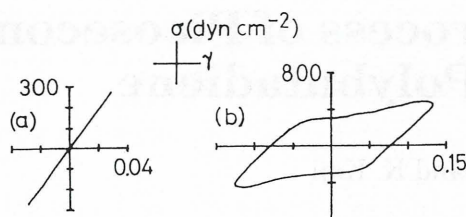
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**Figure 1.** Stress-strain patterns at  $\omega = 0.0524 \text{ s}^{-1}$  obtained for a 20wt% C14 solution of a SB diblock copolymer ( $M_S = 16K$ ,  $M_B = 36K$ ).

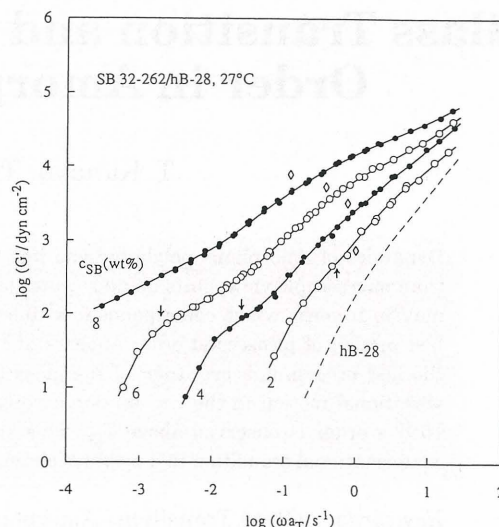
cycle of oscillatory strain. The plasticity of the solution is confirmed also in its steady flow behavior [1,2].

Small angle x-ray scattering (SAXS) measurements indicate that the plasticity of SB copolymer micellar solutions is due to a regular, cubic lattice of the micelles [1,2]. This lattice, called a macrolattice, does not flow but deforms elastically for stresses smaller than the lattice strength (yield value), thereby providing plasticity to the solution.

The macrolattice formation is considered to result from compromise of contradicting thermodynamic requirements, an osmotic requirement for maintaining uniform B segment concentration profile in the C14 matrix phase and an elastic requirement of randomized B block conformation [1,2]. This hypothesis is confirmed from several experimental facts, including a fact that the micelles are preserved but the macrolattice is disordered in polymeric B-selective solvents, homo-B (hB) chains [1,2]: In the SB/hB blends, the uniform B segment concentration profile in the matrix is maintained irrespective of the B block conformation and the two requirements are no longer contradicting with each other.

As explained above, the SB/hB blends contain randomly dispersed micelles and exhibit linear viscoelastic relaxation characterized with elliptic  $\sigma$ - $\gamma$  patterns, as is the case also for homopolymer systems [1-3]. However, the relaxation behavior of the blends is not very similar to that of homopolymers. As an example, Figure 2 shows frequency dependence of storage moduli  $G'$  for a series of SB/hB blends with the SB concentration as indicated [3]. The sample code numbers indicate molecular weights in unit of 1000. The SB micelles exhibit fast and slow relaxation processes (cf. diamonds and arrows) at time scales where the matrix hB has relaxed (dashed curve).

For the fast process, the reduced dynamic moduli scaled with the B block molecular weight  $M$  and concentration  $c$ ,  $G_r = [M/c]G^*$ , exhibit universal relaxation mode distribution [3]. In addition, for concentrated micelles entangled through their B blocks, the relaxation time for the fast process increases exponentially with increasing  $c$  and  $M$  [3]. These features are similar to those for relaxation of branched homopolymers (stars), suggesting that the fast process of the micelles are attributed to relaxation of



**Figure 2.** Frequency dependence of storage moduli for a series of SB/hB blends with the SB concentration as indicated.

individual corona B blocks. This assignment is strongly supported from results of stress relaxation measurements that a damping function for the fast process is in good agreements with the functions for homopolymer systems [4]. However, quantitatively, the relaxation time of the B blocks is  $10^3$ - $10^5$  times longer than that of the corresponding star hB chains [3]. Analysis in terms of tube model suggests that the spatial confinement for the B blocks due to the impenetrable S cores (not existing for star hB) is the main cause for this quantitative difference in the relaxation times [3].

For the slow relaxation process of the micelles, the reduced moduli  $G_r$  do not exhibit the universal mode distribution [3]. In addition, in the nonlinear stress relaxation behavior, the slow process exhibits much stronger damping as compared to the fast process [4]. These facts indicate that the two processes have different molecular origins. For entangled micelles the relaxation time for the slow process was close to an estimated Stokes-Einstein (SE) diffusion time, suggesting that the slow process reflects motion of the micelle as a whole [3]. However, for dilute and nonentangled micelles, the relaxation time for this process is much shorter than the SE diffusion time [3]. The mechanism of the slow process for this case is now being investigated.

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# Glass Transition and Fast Process of Picosecond Order in Amorphous Polybutadiene

T. Kanaya, T. Kawaguchi and K. Kaji

Dynamics of amorphous polybutadiene has been investigated near the glass transition temperature  $T_g$  from microscopic viewpoints using a quasielastic neutron scattering technique in an energy range of 0.01 meV to 10 meV, which corresponds to a time range of  $\sim 4 \times 10^{-10}$  to  $\sim 4 \times 10^{-13}$  s. It was found that a very fast motion of picosecond order appears at the so-called Vogel-Fulcher temperature  $T_0$ , suggesting that the fast process is a precursor of the glass transition. This *fast process* has been assigned to a damped vibrational motion in the C-C torsional potential well. In addition to the *fast process*, a slow motion of  $10^{-10}$  s order is observed above  $T_g$ . This slow process has been assigned to an elementary process of conformational transition in a polymer chain, leading to structural relaxation above  $T_g$ .

**Keywords:** Glass Transition / Amorphous polybutadiene / Neutron scattering / Vogel-Fulcher temperature / Fast process of picosecond order / Damped vibrational motion

Glass transition is one of the most important phenomena in polymer science as well as in materials science because various properties of polymers such as thermal and mechanical properties change drastically below and above the glass transition temperature  $T_g$ . Therefore, lots of investigations have been made on amorphous polymers using various kinds of methods. Most of the investigations have been performed in macroscopic or mesoscopic time and spatial scales using thermal, mechanical and dielectric measurements. Stimulated by the recent microscopic theory, the so-called mode coupling theory (MCT) [1], lots of microscopic measurements have been made on various kinds of glass-forming materials such as organic and inorganic materials and polymers using quasielastic neutron and light scattering, NMR and dielectric relaxation techniques. From microscopic viewpoints, contributions of quasielastic neutron scattering are outstanding. One of the most important contributions is a find-

ing of the *fast process* of picosecond order, which has been observed for most glass-forming materials so far studied. We will report the characteristic features of the *fast process* of picosecond order for cis-1,4-polybutadiene having no side groups, and discuss the role in the glass transition phenomena [2-5].

Figure 1 shows the dynamic scattering laws  $S(Q, \omega)$  observed with an energy resolution of  $\sim 0.2$  meV in a temperature range of 50 K to 260 K covering the glass transition temperature  $T_g$  ( $\sim 170$  K). A very broad excitation peak, the so-called *low-energy excitation* peak, is observed at  $\sim 1.7$  meV at low temperatures somewhat below  $T_g$ . The *low-energy excitation* is a universal feature for all amorphous materials so far examined and believed to be an origin of anomalous excess heat capacity of amorphous materials at low temperatures. The intensity of the *low-energy excitation* increases according to the Bose-Einstein population factor at low temperatures, indicating that the motion is vibrational.

## FUNDAMENTAL MATERIAL PROPERTIES — Polymer Materials Science —

### Scope of research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with the intention of solving fundamentally important problems in polymer science. The main projects are: the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; formation process and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.



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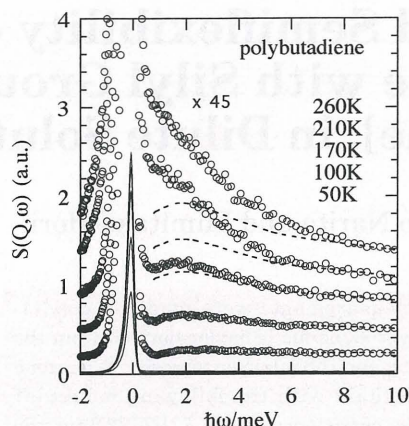
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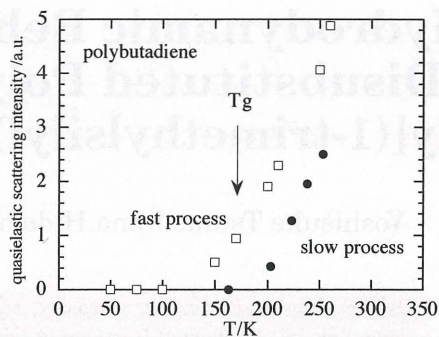
**Figure 1.** Dynamic scattering laws  $S(Q, \omega)$  of polybutadiene. Dashed lines are the expected spectra from the Bose factor.

The dashed lines in the figure are the expected spectra calculated by applying the Bose-Einstein factor to the spectra at 50K; as seen in the case at 100K, the expected spectra agree well with the observed ones while above 120 K some excess quasielastic scattering is observed in an energy range below  $\sim 4$  meV and the intensity increases with temperature. This excess quasielastic scattering is caused by the *fast process*.

The appearance of the *fast process* above  $\sim 120$  K involve an anomalous excess decrease of the elastic scattering intensity, which is the counter part of the quasielastic scattering, indicating that the onset temperature of the *fast process* is  $\sim 120$  K, i.e.,  $\sim 50$  K below  $T_g$ . In Figure 2, the excess quasielastic scattering intensity is plotted against temperature  $T$ , confirming that the onset temperature of the *fast process* is  $\sim 120$  K. It should be emphasized that the temperature 120K corresponds to the so-called Vogel-Fulcher temperature  $T_0$ , which is 50 K below  $T_g$  for most amorphous polymers. The temperature  $T_0$  is sometimes called as the "ideal" glass transition temperature, i.e., an experimentally inaccessible temperature in the limit of infinitely slow cooling. The value of  $T_0$  is not affected by the time scale of the experiment, whereas the calorimetric glass transition temperature depends on the time scale. Therefore,  $T_0$  is considered to be a fundamental property of the sample. The present result implies that quasielastic neutron scattering can directly detect the temperature  $T_0$  and strongly suggests that the *fast process* is a precursor of the glass transition phenomena.

In order to see the nature of the *fast process*, its characteristic time  $\tau_f$  was evaluated from the spectral width, which was plotted against the length of the scattering vector  $Q$  for 210 and 260K. The characteristic time  $\tau_f$  of picosecond order was almost independent of  $Q$  and  $T$ , suggesting that the *fast process* is a localized motion. The activation energy of  $\tau_f$  evaluated for the melt was  $\sim 0.5$  kcal/mol, which is very small compared with the energy barrier height of the C-C torsional potential ( $2\sim 3$  kcal/mol), indicating that the *fast process* is not related to the conformational transition between rotational isomeric states (trans and gauche). In other words, the atomic groups or segments are trapped within the C-C torsional potential even above the onset temperature of the *fast process*. In this sense, the *fast process* can be called a cage motion. At a very low temperature, such motion must be vibrational but near  $T_g$  it is damped by thermal agitations. At the present stage, we conclude that the *fast process* is a damped vibrational motion in the C-C torsional potential well.

In the low energy range of 0.01 meV to 0.2 meV, a



**Figure 2.** Temperature dependence of quasielastic scattering intensity of the fast and slow processes.

new relaxational motion of  $10^{-10}$  s order appeared as a quasielastic scattering above the glass transition temperature  $T_g$ . The motion is termed the *slow process*. The onset temperature of the *slow process* is around the glass transition temperature  $T_g$  (see Figure 2). The characteristic time  $\tau_s$  of the *slow process* depended on  $T$  in contrast to the *fast process* and the activation energy was  $\sim 2.9$  kcal/mol. This value corresponds to the C-C torsional potential barrier height, indicating that the *slow process* includes an elementary process for conformational transition between rotational isomeric states such as trans and gauche, which leads to the structural relaxation above  $T_g$ . It is emphasized that the *slow process* must be assisted by the damped vibrational motion in the C-C torsional potential well (the *fast process*).

Similar results were obtained for trans-1,4-polychloroprene [6] which has no side groups. On the other hand, polymers with side groups or internal degrees of freedom such as polystyrene [7-9] and polycarbonate [10] show similar *fast processes* of picosecond order far below  $T_g$ . In the case of polystyrene, the *fast process* far below  $T_g$  has been assigned to phenyl ring motions using a deuterium labeling method [7,9]. Generally, it is rather difficult to distinguish the *fast process* of side groups from that of main chains. At the present stage, therefore, the picture presented here is valid only for polymers without side groups. Further investigations are now in progress.

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# Hydrodynamic Behavior and Semiflexibility of a Disubstituted Polyacetylene with Silyl Group, Poly[(1-trimethylsilyl)-1-propyne], in Dilute Solution

Yoshisuke Tsunashima, Hideyuki Hara, Hidehiro Narita and Fumitaka Horii

Dynamic light scattering, viscosity, sedimentation velocity measurements were made on poly[(1-trimethylsilyl)-1-propyne] fractions in benzene and THF. The hydrodynamic behavior derived from the diffusion and sedimentation coefficients, the internal mode motions, and the intrinsic viscosity in benzene at 30°C indicated that the present polymer is a semiflexible chain with the following molecular parameters expressed in terms of the wormlike cylinder model; the persistence length  $\lambda^{-1/2}=32.5\text{nm}$ , the molecular mass per unit contour length  $M_L=400\text{nm}^{-1}$ , and the cylinder diameter  $d=1.1\text{nm}$ .

**Keywords:** Polyacetylene derivatives/ Semiflexible chain/ Dynamic light scattering/ Translational diffusion coefficient/ Sedimentation coefficient/ Intrinsic viscosity

Although polyacetylene is virtually insoluble in any solvent, the disubstituted polyacetylenes in which two hydrogens are replaced by alkyl and phenyl groups are soluble in ordinary organic solvents and show solution behavior characteristic of the semiflexible polymers. Poly[(1-trimethylsilyl)-1-propyne] (PMSP) is a disubstituted polyacetylene which contains the silyl group instead of phenyl one;  $-\text{[C(CH}_3\text{)=C(Si(CH}_3\text{)}_3\text{)]}_n-$ . This polymer is in the glassy state at room temperature but has extremely high permeability for various gases in the solid film[1]. These features are distinguished clearly from those of usual disubstituted polyacetylenes, suggesting steric effects and high molecular mobility due to the silyl group. Since PMSP dissolves in benzene and

THF (good solvents), it is interesting to compare the solution behavior with that of an usual disubstituted polyacetylene, poly(1-phenyl-1-propyne) ( $-\text{[C(CH}_3\text{)=C(C}_6\text{H}_5\text{)]}_n-$ , PPP), which shows the semiflexibility even in a good solvent, toluene[2].

The PMSP sample, a gift from Prof. T. Masuda, Kyoto University, was separated into 14 fractions by repeated precipitation fractionations in benzene-methanol mixtures and freeze-dried from filtered benzene solutions. Their hydrodynamic characteristics were determined through dynamic light scattering, sedimentation, and viscosity experiments in benzene at 30°C: the translational diffusion coefficient  $D$ , the sedimentation coefficient  $s$ , their first concentration-dependence coefficients (the hydrodynamic virial

## FUNDAMENTAL MATERIAL PROPERTIES — Molecular Motion Analysis —

### scope of research

*The research activities in this subdivision cover structural studies and molecular motion analyses of polymers and related low molecular weight compounds in the crystalline, glassy, liquid crystalline, and solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.*



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coefficients)  $k_D$  and  $k_S$ , the intrinsic viscosity  $[\eta]$ , and the decay rates for the dynamical modes of motions  $\Gamma_i$  ( $i=1,2$ ) were analyzed.

When  $D$  and  $s$  are expanded in a series of the polymer mass concentration  $c$  about the infinite dilution values  $D_0$  and  $s_0$ , i.e.,  $D=D_0(1+k_Dc)$  and  $s^{-1}=s_0^{-1}(1+k_Sc)$ , the coefficients  $k_D$  and  $k_S$  represent the hydrodynamic and/or thermodynamic interactions of the polymers and are related by the relation  $k_D+k_S=2A_2M_W$  to the second virial coefficient  $A_2$ , a measure of the thermodynamic intermolecular interactions. Here  $M_W$  denotes the weight-average molecular weight of the polymer. As typically shown by  $k_D=-311$  and  $k_S=314$   $\text{cm}^3\text{g}^{-1}$  for fraction 4 of PMSP ( $M_W=6.98 \times 10^5$ ),  $A_2$  of PMSP was found to be zero to within experimental errors, indicating little intermolecular excluded volume effects. This means that PMSP is in the unperturbed state in benzene at  $30^\circ\text{C}$ . However,  $[\eta]$  did not show the linear relation between  $[\eta]$  and  $M_W^{1/2}$ , as should be for the unperturbed chains. Rather, the plot of  $(M_W^2/[\eta])^{1/3}$  against  $M_W^{1/2}$  (Bohdanecky plot, Fig.1) was found to be linear in all the region of  $M_W$  measured, the intercept being not equal to zero but positive definite. PMSP in benzene at  $30^\circ\text{C}$  is thus a semiflexible polymer and the intramolecular excluded volume interactions were not appreciable at  $M_W$  up to  $7 \times 10^5$ .

The semiflexible chain parameters of PMSP were estimated by analyzing the viscosity data in terms of a wormlike cylinder model of the diameter  $d$ , the persistence length  $\lambda^{-1/2}$ , the contour length  $L$ , and the molecular mass per unit contour length  $M_L=M_W/L$ . The Bohdanecky expression for  $[\eta]$ ,  $(M_W^2/[\eta])^{1/3} = A + BM_W^{1/2}$ , gives the parameters  $M_L$  and  $\lambda^{-1}/M_L$  with  $A=A_0M_L\Phi_\infty^{-1/3}$ ,  $B=B_0(\lambda^{-1}/M_L)^{1/2}$  and  $A_0$  and  $B_0$  the function of  $d/\lambda^{-1}$ . Adopting the diameter  $d=1.1 \pm 0.2\text{nm}$  from the crystallographic data of polyacetylene and  $\Phi_\infty=2.17 \times 10^{23}\text{mol}^{-1}$ , we obtained the chain parameters of PMSP to be  $\lambda^{-1/2}=3.25\text{nm}$  and  $M_L=400\text{nm}^{-1}$ . In Table 1 these values are compared with those of PPP and typical cellulose derivatives, i.e., cellulose acetate (CA) and hydroxypropyl cellulose (HPC)[3]. The axial ratio of Kuhn segment  $X_k=\lambda^{-1}/d=5.9$  for PMSP in benzene is smaller than that of PPP in toluene, 6.9, indicating that PMSP behaves as a wormlike chain but its rigidity is lower than that of the phenyl-substituted polyacetylene, PPP, as well as the usual cellulose derivatives in dimethylacetamide(DMAc). In Figure 2 is shown the scattering vector ( $q$ ) dependence of the first cumulant  $\Gamma_e$  for PMSP in benzene at  $30^\circ\text{C}$ .  $\Gamma_e$ , the decay rate of the scattered-intensity time-correlation function at time  $\rightarrow 0$ , gives us information on whole modes of motions in the wormlike chain, i.e., the translational diffusion, the rotational diffusion, the anisotropy of the transla-

tional diffusion, the internal modes of motions and so on.  $\Gamma_e/D_0q^2$  increases gradually with increasing  $qL$ . However, it never approaches to a plateau, the characteristic feature of rigid rods, and deviates upward drastically. This deviation seems to exceed the behavior of typical wormlike chains of high stiffness (a chain line) and indicates that the intrachain flexibility becomes effective. These double-stepped increase of  $\Gamma_e/D_0q^2$  with increasing  $qL$  certifies that PMSP in

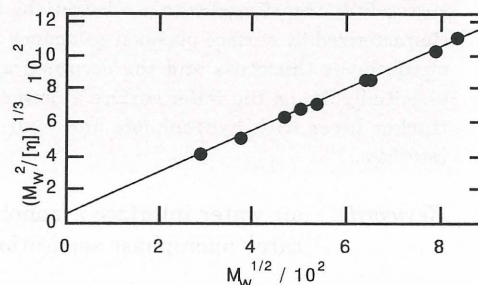


Figure 1. Bohdanecky plot for PMSP in benzene at  $30^\circ\text{C}$ .

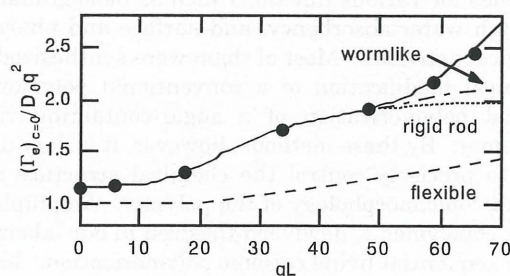


Figure 2. Plot of  $(\Gamma_e)_{c=0}/D_0q^2$  vs.  $qL$  for PMSP in benzene at  $30^\circ\text{C}$ .

Table 1. Axial ratio for wormlike chain polymers

polymer	solvent	$X_k$	$\lambda^{-1/2}(\text{nm})$	$d(\text{nm})$
PMSP	benzene	5.9	3.3	1.1
PPP	toluene	6.9	3.9	1.1
CA(2.5)	DMAc	17.3	7	0.81
HPC	DMAc	13.5	7	1.04

benzene is a relatively flexible wormlike chain.

We are grateful to Prof. Toshio Masuda for kindly providing us a PMSP sample.

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# Langmuir-Blodgett Films of An Amphiphilic Block Polymer Having Glucose Residues

Yoshinobu Tsujii, Shinpei Yamamoto, Kenji Yamada, Masahiko Minoda,  
Takeshi Fukuda and Takeaki Miyamoto

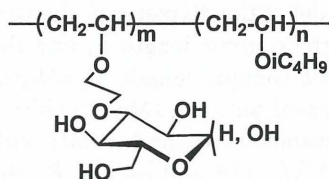
Amphiphilic block polymer **1** with a narrow molecular weight distribution was studied with its monolayer forming properties at the air-water interface. Polymer **1** and its blends with poly(isobutyl vinyl ether) homopolymer were found to form a stable monolayer on the water surface. The surface monolayers were successfully transferred onto a substrate by the Langmuir-Blodgett technique, and the built-up film was characterized by surface plasmon resonance and transmission electron microscopy. The observed values of the layer thickness and the occupied area indicated that the hydrophobic segments, which lie essentially flat on the water surface at lower surface pressures, aggregate at higher pressures, forming a thicker layer with hydrophobic and hydrophilic segments microphase-separated at the air-water interface.

**Keywords:** air-water interface / monolayer formation / structural transition / layered structure / microphase separation / blend LB film

Many studies have been focused on the synthetic polymers with pendant mono- and/or oligo-saccharide residues for various functions such as biodegradability, high water-absorbency, and surface and pharmacological activities. Most of them were synthesized by chemical modification of a conventional polymer or radical polymerization of a sugar-containing vinyl monomer. By these methods, however, it is very difficult to precisely control the chemical structure and macroscopic morphology of the polymer. Amphiphilic block copolymer **1**, newly synthesized in our laboratory by sequential living cationic polymerization,<sup>1)</sup> has a narrow molecular weight distribution of  $M_w/M_n < 1.06$  and a controlled block composition. One of the two blocks of this copolymer consists of hydrophilic

repeating units containing a glucose residue, and the other is a poly(isobutyl vinyl ether) (PIBVE) block, which is hydrophobic. Since PIBVE has a monolayer-forming ability by itself, the block copolymer is expected to be fabricated into a glucose residue-carrying ultrathin film with a supramolecular structure by means of the Langmuir-Blodgett technique.

Polymer **1** with an appropriate segmental compo-



Block Copolymer **1**

P1( $m/n=20/48$ )

P2( $m/n=20/89$ )

## ORGANIC MATERIALS CHEMISTRY — Polymeric Materials —

### Scope of research

Basic studies have been conducted for better understandings of the structure/property or structure/function relations of polymeric materials and development of novel functional polymers. Among those have been the studies on (1) the synthesis and properties of cellulose- and oligosaccharide-based functional polymers, e.g., bio-degradable polymers, liquid crystals and polymers of well-defined structure having pendant oligosaccharides, (2) the structure of polymer gels, ultrathin films and polymer alloys, and (3) the syntheses of new types of block and graft copolymers and fullerene( $C_{60}$ )-including polymers.



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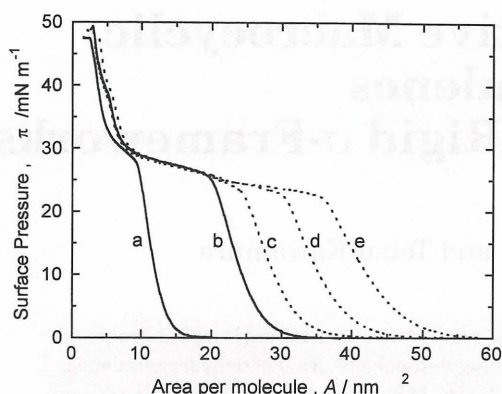
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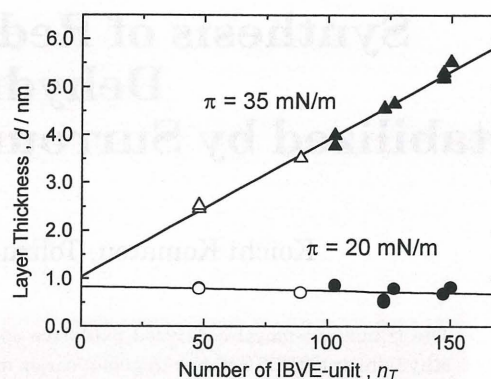


**Figure 1.**  $\pi$  -  $A$  isotherms of the block copolymers, (a) P1 and (b) P2, and the blends, PIBVE/P2 = (c) 0.10, (d) 0.25, and (e) 0.42

sition ( $m/n = 20/48$  or  $20/89$ ), spread from a mixture solution of methanol and chloroform onto the water surface, was found to form a stable monolayer. It was also possible to prepare a blend monolayer by spreading a mixture solution of the block polymer and PIBVE on the water surface. The surface pressure ( $\pi$ ) - occupied area ( $A$ ) isotherm for these surface monolayers measured at 10 °C are given in Figure 1, where  $A$  is the surface area per hydrophilic subchain in all cases. They exhibit a plateau region, suggesting a structural change taking place on the water surface at a specific pressure. With increasing number of the IBVE units in the copolymer and those blended as a homopolymer, the plateau region expands;  $A$  is proportional to  $n_T$  below the plateau pressures, where  $n_T$  is the total number of IBVE units divided by the number of the hydrophilic subchains, while  $A$  is almost constant at pressures above the plateau. From the  $n_T$  dependence of  $A$ , the occupied area per IBVE unit at 20 mN/m (below the plateau) was determined to be 0.25 nm<sup>2</sup>, which is almost equal to the area of IBVE unit evaluated from the space filling molecular model. This means that at low pressures, the IBVE segments lie essentially flat on the water surface, which is consistent with the  $n_T$  dependence of the layer thickness at low pressures (see below).

The surface monolayers were successfully transferred onto a substrate by the vertical dipping method to form a Y-type multilayer film, the thickness of which was determined by surface plasmon resonance<sup>2)</sup> and transmission electron microscopy<sup>3)</sup>. Both below and above the plateau region, proportionality of the total film thickness to the deposit number as well as transfer ratios close to unity were observed, confirming a good transferability of the monolayer. Figure 2 shows the layer thickness  $d$  plotted against  $n_T$ . The layer thickness  $d$  is apparently constant at 20 mN/m, while it increases linearly with increasing  $n_T$  at 35 mN/m.

The above arguments on the  $n_T$  dependence of  $A$  and  $d$  suggest the fine structure of the surface monolayers illustrated in Figure 3; the IBVE segments, which lie essentially flat on the water surface at low pressures, aggregate at higher pressures, forming a



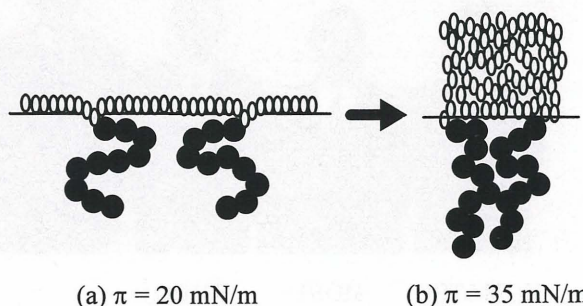
**Figure 2.** Plots of  $d$  vs.  $n_T$  for LB films of the block copolymers (open symbols) and the blends (closed symbols) deposited at 20 and 35 mN/m

thicker layer with hydrophobic and hydrophilic segments microphase-separated at the air-water interface. This is consistent with the fact that the surface pressure of the plateau is almost the same as the collapse pressure (22 mN/m) for the PIBVE homopolymer. According to this model, the layer thickness extrapolated to  $n_T = 0$  (about 1.0 nm; Figure 2) should correspond to that of the glucose residue-carrying hydrophilic segments: it is thus indicated that the LB film deposited at a high pressure consists of the hydrophilic layer with a thickness of 1.0 nm and the hydrophobic layer with a thickness proportional to  $n_T$ .

These results suggest a useful method to control the supramolecular structure of an ultrathin block copolymer film by blending it with a homopolymer; at lower pressures, it is possible to decrease the surface density of the hydrophilic segments in the water, and at higher pressures, where a microphase-separated structure is formed on the water surface (Figure 3b), it is possible to adjust the hydrophobic layer thickness by blending the homopolymer.

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**Figure 3.** Schematic illustration of monolayers at the air-water interface.



# Synthesis of Redox-Active Macrocyclic Dehydroannulenes Stabilized by Surrounding Rigid $\sigma$ -Frameworks

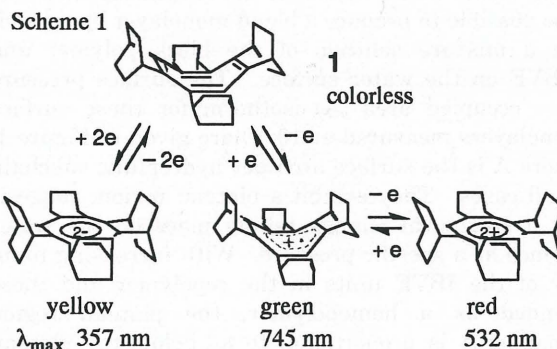
Koichi Komatsu, Tohru Nishinaga, and Tetsu Kawamura

The transition-metal catalyzed oxidative coupling has been applied to 2,3-diethynyl- and 2-bromo-3-ethynylbicyclo[2.2.2]octenes to give a series of macrocyclic conjugated polyenyne, i.e. dehydroannulenes. The X-ray crystallography has demonstrated that the hexadehydro[18]annulene has a completely planar  $\pi$ -system while that of the tetradehydro[16]annulene system is considerably bent. These  $\pi$ -systems are characterized by ready and highly reversible redox behaviors as examined by the use of cyclic voltammetry.

**Keywords:**  $\pi$ -conjugation / macrocycles / X-ray structure / CV / oxidative coupling / Pd catalysis

The highly conjugated  $\pi$ -electronic systems are of particular interest from the viewpoint of their possible applicability for functionality materials. Fundamental studies on the redox properties of these systems are important since the redox behaviors can trigger various physicochemical events that are required for application of these materials.

Previous studies in our group demonstrated that a cyclooctatetraene fully annelated with bicyclo[2.2.2]octene units (**1**) is redox active, affording not only a 10- $\pi$  aromatic dianion but cation radical [1] and dication [2], which are the first examples of cationic species of cyclooctatetraene stable at room temperature. While the neutral compound is colorless, each of the ionic species exhibits deep colors



characteristic to their ionic state as shown in Scheme 1.

Now this work has been extended to the synthesis

## ORGANIC MATERIALS CHEMISTRY — High-Pressure Organic Chemistry —

### Scope of Research

Fundamental studies are being made for creation of new functional materials with novel structures and properties and for utilization of high pressure in organic synthesis. The major subjects are: synthetic and structural studies on novel cyclic  $\pi$ -systems; chemical transformation of fullerene  $C_{60}$ ; utilization of carbon monoxide and dioxide for organic synthesis under the transition-metal catalysis.



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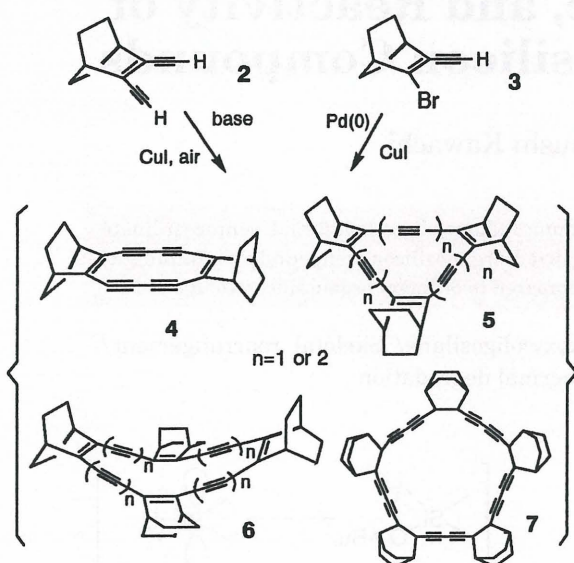
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Scheme 2



of compounds with more expanded  $\pi$ -systems, i.e., a series of dehydroannulenes containing the bicyclo[2.2.2]octene frameworks.

As shown in Scheme 2, the oxidative coupling of enediyne **2** and careful separation using GPC afforded a series of cyclomers, the dehydroannulenes, **4** (red crystals, 15%), **5** (n=2) (orange needles, 55%), **6** (n=2) (yellow solid, 0.6%), and **7** (red-brown crystals, 2%). Also the Pd-catalyzed coupling of enyne **3** gave trimer **5** (n=1) (red crystals, 22%) and tetramer **6** (n=1) (yellow needles, 9%).

The X-ray crystallography clearly demonstrated the presence of a planar  $\pi$ -conjugated system in **5** (n=2) and a bent and bond alternating cyclohexadeca-1,5,9,13-tetraene-3,7,11,15-tetrayne system in **6** (n=1) as shown in Figure 1.

The redox behaviors on these macrocyclic  $\pi$ -systems were examined by the use of cyclic voltammetry to give the results summarized in Table 1. Several

Table 1. Redox Potentials of Annulenes **4**, **5**, and **6**<sup>a</sup>.

Compd	$E_{ox}^2$	$E_{ox}^1$	$E_{red}$
<b>4</b>		(+0.93) <sup>b</sup>	-1.67
<b>5</b> (n=1)	(+0.99) <sup>b</sup>	+0.54	-1.93
<b>6</b> (n=1)	(+0.88) <sup>b</sup>	+0.62	-1.96
<b>5</b> (n=2)		(+1.21) <sup>b</sup>	-1.87
<b>6</b> (n=2)			-1.53

<sup>a</sup> In PhCN with 0.1 M TBAP; sweep rate 0.1 V s<sup>-1</sup>.

<sup>b</sup> Peak potential of the irreversible peak.

characteristic features emerge from these data. For example, both of the antiaromatic 4n  $\pi$ -electronic systems **5** (n=1) and **6** (n=1) undergo ready and completely reversible one-electron oxidation at remarkably low potential such as +0.5 ~ +0.6 V vs Ag/AgNO<sub>3</sub>. Particularly in comparison with its mother compound having no substituent, the redox potentials of the hydrocarbon **5** (n=1) are cathodically shifted in general, reflecting the electron-donating tendency of the annelated bicyclo[2.2.2]octene units. It is also to be noted that, in spite of such electronic effects of the bicyclic frameworks, the expansion of the  $\pi$ -conjugated system is reflected in the occurrence of reversible one-electron reduction, which was not observed in the case of corresponding cyclic  $\pi$ -systems without acetylenic bonds.

Further study is now under way to elucidate the possibility of these macrocyclic polyyne to exhibit selective complexation ability with metal ions or with specific organic molecules.

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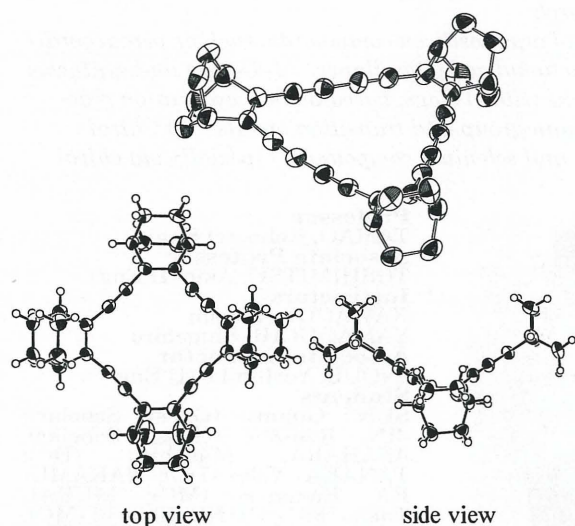


Figure 1. X-Ray crystal structures of **5** (n=2) (top) and of **6** (n=1) (bottom).



# Preparation, Structure, and Reactivity of Functionalized Organosilicon Compounds

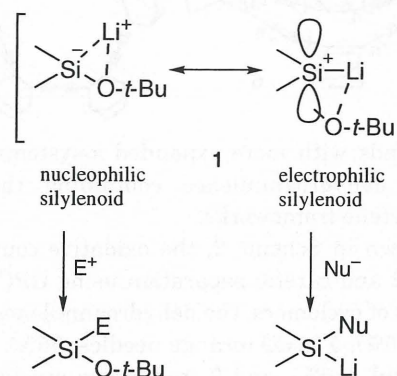
Kohei Tamao and Atsushi Kawachi

Preparation, structure, and reactivity of (alkoxysilyl)lithium, (alkoxy)oligosilanes, and pentacoordinate alkoxydisilane have been investigated. These functionalized organosilicon compounds containing a heteroatom substituents exhibit remarkable reactivities compared to ordinary organosilicon compounds.

**Keywords:** (Alkoxysilyl)lithium / Silylenoid / (Alkoxy)oligosilane / Skeletal rearrangement / Silylene / Pentacoordinate disilane / Thermal degradation

## (1) The Chemistry of Silylenoids: Preparation and Reactivity of (Alkoxysilyl)lithium [1]

We report the first results of silylenoid chemistry, analogous to carbenoid chemistry. (*t*-Butoxysilyl)lithium (*t*-BuO)Ph<sub>2</sub>SiLi (**1**) prepared from (*t*-butoxysilyl)stannane with *n*-BuLi in THF is stable at -78 °C. In the presence of 12-crown-4, **1** is stable as silyl anion even at 0 °C and reacts with electrophiles only. In contrast to this, **1** exhibits the ambiphilic reactivity and undergoes at 0 °C self-condensation smoothly to form (*t*-BuO)Ph<sub>2</sub>SiPh<sub>2</sub>SiLi or butylation in the presence of an excess amount of *n*-BuLi and TMEDA to form *n*-BuPh<sub>2</sub>SiLi. The ambiphilic reactivities of **1** could be accounted for by contribution of two extreme structures, that is, a nucleophilic silyl anionic structure and an electrophilic silylenoid structure. In the latter, the electropositive lithium atom bound to silicon ionizes and activates the silicon-oxygen bond so that the silicon becomes susceptible to the nucleophilic attack.



## (2) Palladium-Catalyzed Skeletal Rearrangement of (Alkoxy)oligosilanes via Silylene-Transfer [2]

Poly(alkoxy)trisilanes and tetrasilanes have been found to undergo clean skeletal rearrangement in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst at 80 - 140 °C in the fashion that the internal silylene moiety is transferred to the terminal positions. Ten substrates have

## SYNTHETIC ORGANIC CHEMISTRY — Synthetic Design —

### Scope of research

(1) Synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds, functionalized silyl anions, and functionalized oligosilanes. (2) Design and synthesis of novel  $\pi$ -conjugated polymers containing silacyclopentadiene (silole) rings, based on new cyclization reactions and carbon-carbon bond formations mediated by the main group and transition metals. (3) Chiral transformations and asymmetric synthesis via organosulfur and selenium compounds, especially via chiral episulfonium and episelenonium ions.



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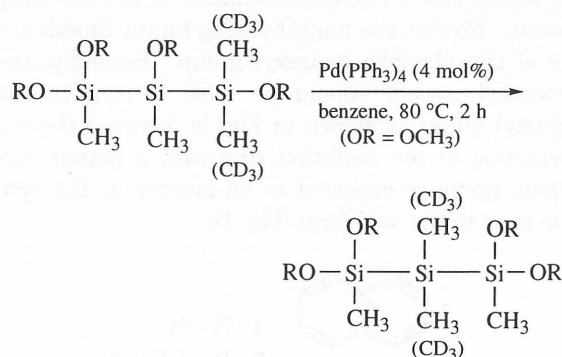
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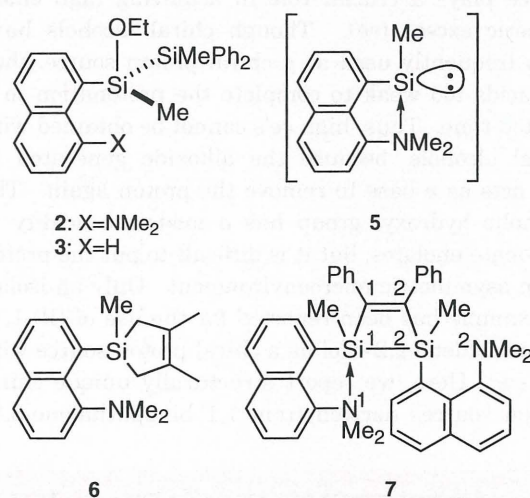
been examined. Typically, 1,2,2,3-(MeO)<sub>4</sub>Me<sub>4</sub>Si<sub>3</sub>, 1,1,2,3-(MeO)<sub>4</sub>Me<sub>4</sub>Si<sub>3</sub>, 1,2,3-(MeO)<sub>3</sub>Me<sub>5</sub>Si<sub>3</sub>, and 1,2-(MeO)<sub>2</sub>Me<sub>6</sub>Si<sub>3</sub>, are converted into the 1,1,1,3-, 1,1,3,3-, 1,1,3-, and 1,1-isomers, respectively, in quantitative yields: the reactivity decreases roughly in this order. In a deuterium-labeled study, 1,1,2,3-(MeO)<sub>4</sub>-3,3-(CD<sub>3</sub>)<sub>2</sub>Me<sub>2</sub>Si<sub>3</sub> gives 1,1,3,3-(MeO)<sub>4</sub>-2,2-(CD<sub>3</sub>)<sub>2</sub>-Me<sub>2</sub>Si<sub>3</sub> exclusively, no CD<sub>3</sub>/CH<sub>3</sub> random exchange being observed. A tetrasilane 1,2,3,4-(MeO)<sub>4</sub>Me<sub>6</sub>Si<sub>4</sub> is also transformed into the 1,1,4,4-isomer. A proposed mechanism involves silylene-transfer from the internal position to the terminal position(s) through the following key steps: oxidative addition of the Si-Si bond to Pd(0) and subsequent  $\alpha$ -elimination to a bis(silyl)(silylene)Pd complex, stabilized by the intramolecular coordination of alkoxy group(s) to the silylene center. The novel skeletal rearrangement may be useful for the structural modification of polyfunctionalized polysilanes of much current interest.



### (3) Remarkably Facile Thermal Generation of Silylene from a Pentacoordinate Alkoxydisilane and Its Trapping as a Pentacoordinate 1,2-Disilacyclobut-3-ene [3]

Pentacoordinate ethoxydisilane **2**, which contains the 8-dimethylamino-1-naphthyl group and the ethoxy group on the same silicon atom, and the tetra-coordinate counterpart **3** have been prepared. The X-ray structure analysis of **2** reveals that the geometry of the particular silicon atom is deformed from tetrahedral to pseudo-trigonal bipyramidal with the ethoxy group and the amino group at two pseudo-apical positions, having the N1...Si1 distance 2.969(3) Å and the N1...Si1-O1 angle 171.36(9)°. This compound has a normal Si1-Si2 distance 2.368(1) Å, a slightly

long Si-O bond 1.665(2) Å and a small O-Si-Si bond angle 97.35(8)°. The two methyl groups on nitrogen in **2** appear as diastereotopic two separate singlets in <sup>1</sup>H and <sup>13</sup>C NMR spectra at room temperature. **2** undergoes thermal degradation readily at 90°C in DMF or 110 °C in toluene to form EtOSiPh<sub>2</sub>Me (**4**) in high yields, while **2** is stable under similar conditions. The silylene species **5** is trapped efficiently with 2,3-dimethyl-1,3-butadiene and diphenylacetylene to form the corresponding adducts **6** and **7**, respectively. The X-ray structure analysis reveals that **7** is the first example of a pentacoordinate 1,2-disilacyclobut-3-ene and involves two different conformations of the 8-dimethylamino-1-naphthyl groups as shown below. The Si1 is highly pentacoordinated, with the N1...Si1 distance 2.789 (3) Å, while the N2...Si2 is long 3.039(3) Å, causing the 1,2-disilacyclobutene ring unsymmetrical with different bond lengths Si1-C1 1.932(3) Å and Si2-C2 1.891(3) Å. Compound **7** is oxygen-stable.



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# Enantioselective Protonation of Enolates: Novel Chiral Proton Sources and Remarkable Effects of the Counter Cation<sup>1</sup>

Kaoru Fuji, Takeo Kawabata, Akio Kuroda and Tooru Taga

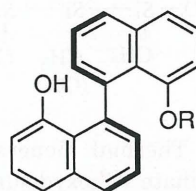
New chiral proton sources 2-4 having axial chirality were introduced. They protonate 2-alkyl  $\alpha$ -tetralone enolates 8-10 enantioselectively. Enantiomeric excess of up to 94% was obtained on protonation of 10, when  $-MgI$  was used as a counter cation.

**Keywords:** Asymmetric synthesis / Protonation / Magnesium enolate

Enantioselective protonation<sup>2</sup> of ketone or ester enolates constitutes an important method for the preparation of optically active  $\alpha$ -substituted ketones or esters, complementary to the asymmetric  $\alpha$ -alkylation of carbonyl compounds. The acidity of the proton source plays a crucial role in achieving high enantiomeric excess (ee). Though chiral alcohols have been frequently used as a chiral proton source, they are acids too weak to complete the protonation in a limited time. Thus, high ee's cannot be obtained with chiral alcohols, because the alkoxide generated in situ acts as a base to remove the proton again. The phenolic hydroxyl group has a moderate acidity to protonate enolates, but it is difficult to put the proton in an asymmetric microenvironment. Only an isolated example has been reported for the use of (R)-1,1'-binaphthalene-2,2'-diol as a chiral proton source with low ee.<sup>3</sup> Here, we report structurally unique chiral proton sources derived from 1,1'-binaphthalene-8,8'-

diol (1) and a remarkable effect of  $Mg(II)$  on enantioselective protonation.

We chose carbamate 2-4 as the chiral proton sources, in which the acidic hydrogen would be kept in a highly chiral microenvironment for the following reasons. Firstly, the naphthyl ring totally blocks one side of the phenolic hydroxyl group. Secondly, the carbamoyl moiety should be fixed as syn to the hydroxyl group as shown in Fig. 1a, because the  $\pi$ - $\pi$  interaction of the naphthyl ring with a planar carbamoyl group is expected to be greater in the syn-form than in the anti-form (Fig. 1b).



- 1 : R = H
- 2 : R = CONMe<sub>2</sub>
- 3 : R = CONEt<sub>2</sub>
- 4 : R = CON<sup>i</sup>Pr<sub>2</sub>

## SYNTHETIC ORGANIC CHEMISTRY — Fine Organic Synthesis —

### Scope of Research

*The research interests of the laboratory include the development of new synthetic methodology, molecular recognition, and design and synthesis of biologically active compounds including functionalized DNA oligomers. Programs are active in the areas of use of chiral leaving groups for an asymmetric induction, desymmetrization of symmetrical compounds, asymmetric alkylation of carbonyl compounds based on "memory of chirality", use of binaphthalenes in the asymmetric synthesis and chiral recognition, and antitumor diterpenoids.*



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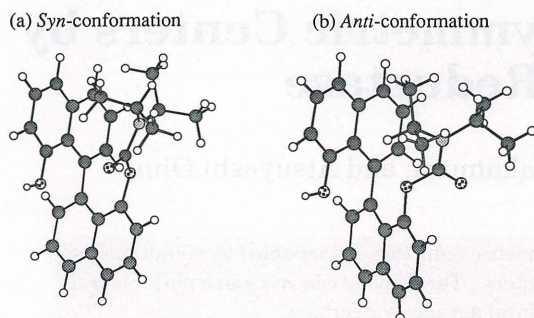
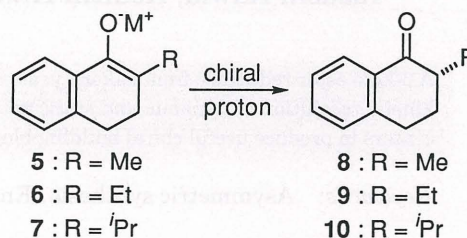


Figure 1.

Racemic **1** was resolved through the diester of (*S*)-*O*-acetylmandelic acid to give optically pure (*R*)-**1**. The desired carbamates **2-4** were easily prepared by condensation with the corresponding carbamyl chloride. X-ray analysis of (*R*)-**4** unexpectedly revealed that the orientation of the carbonyl group is anti to the hydroxyl group in the crystalline state (Fig. 1b) due to intermolecular hydrogen bonding. Molecular mechanics (MM) calculations,<sup>4</sup> however, predict that **4** exists in the *syn*-form as the lowest energy conformation (Fig. 1a), which is 4.2 kJ/mol lower than that of *anti*-form of the lowest energy. This contradiction is not surprising, because intermolecular interactions are not included in the calculations. The conformation of (*R*)-**4** in solution would be similar to that from the calculations rather than that in the crystalline state, since such a strong intermolecular hydrogen bonding observed in the crystalline state would not be expected in the solution.

Pertinent results of chiral protonation of enolates **5-7** are listed in Table I. The magnesium enolates were prepared from the corresponding enol acetates with methyl Grignard reagent in ether at room temperature. The enolates were protonated with a suspension of optically active carbamates **2-4** in ether at -78°C for 0.5 h followed by warming to 10°C for 1 h. The bulkiness of the substituents on the nitrogen has

little effect on ee (see entries 1, 3, and 4). The MM calculations indicated that carbamates **2** and **3** exist in essentially the same conformation as that of **4**. This might support the observed results of the small effect of the substituents on the nitrogen atom.



A remarkable effect of a counter cation of the enolate was observed. Magnesium enolate gave a higher ee than those of lithium (entries 1 and 2, 7 and 8, 9 and 10). Although the profound effects of the counter cation on the diastereoselectivity are well known in the aldol condensations, such a marked effect of the counter cation has not been observed in the asymmetric protonation. In the case of **8**, the lithium enolate gave a product with an absolute configuration opposite to that from the magnesium enolate (see entries 1 and 2). It is clear that the aggregation state of lithium enolate is different from that of magnesium, which should play a key role toward the observed effects. Although more detailed studies are necessary to gain insight into the precise mechanism, the transition model shown in Fig. 2a accounts for the observed *S*-configuration of product **13**. Another transition state 2b giving *ent*-**13** would be highly unfavorable due to a severe repulsive interaction between the isopropyl group and the naphthyl moiety.

In conclusion, we have introduced novel chiral proton sources with unique structural features and shown that they can protonate the magnesium enolate of 2-alkyltetralones with moderate to high ee. The present studies raise the important suggestion that a change in the counter cation might be the way to achieve a high degree of enantioselective protonation, even though structural modification of chiral proton sources is very important.

Table 1.

entry	enolate <sup>a</sup> compound	M =	proton source	product	yield <sup>b</sup>	% ee <sup>c</sup>
1	<b>5</b>	MgI	<b>2</b>	<b>8</b>	57(73)	58
2	<b>5</b>	Li	<b>2</b>	<i>ent</i> - <b>8</b>	66	10
3	<b>5</b>	MgI	<b>3</b>	<b>8</b>	72(80)	69
4	<b>5</b>	MgI	<b>4</b>	<b>8</b>	66(73)	54
5	<b>6</b>	MgI	<b>2</b>	<b>9</b>	73(84)	67
6	<b>6</b>	MgI	<b>3</b>	<b>9</b>	84(96)	75
7	<b>7</b>	Li	<b>2</b>	<b>10</b>	72	9
8	<b>7</b>	MgI	<b>2</b>	<b>10</b>	48(90)	92
9	<b>7</b>	Li	<b>3</b>	<b>10</b>	74	15
10	<b>7</b>	MgI	<b>3</b>	<b>10</b>	71(81)	90

<sup>a</sup>Prepared from the corresponding enol acetate with MeMgX unless otherwise stated. <sup>b</sup>The yield in the parenthesis is based on the recovered starting material. <sup>c</sup>Determined by HPLC using a chiral column (Daicel Chiralpack AS).

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4. The MacroModel/MM2 (version 4.0) force field was used.



# Introduction of Plural Asymmetric Centers by a $\beta$ -Keto Ester Reductase

Yasushi Kawai, Kouichi Hida, Kaoru Nakamura, and Atsuyoshi Ohno

A  $\beta$ -keto ester reductase from bakers' yeast catalyzes asymmetric reduction accompanied by simultaneous kinetic resolution of dynamic and static optically active centers. The enzyme can recognize plural chiral centers to produce useful chiral building blocks containing plural asymmetric carbons.

**Keywords:** Asymmetric synthesis / Enzyme / Reductase / Chiral  $\beta$ -hydroxy ester

A number of purified alcohol dehydrogenases are now commercially available and used widely for the reduction of ketones to obtain chiral alcohols. The optically active alcohols are employed as useful chiral starting materials for the syntheses of biologically active compounds. In most cases so far reported, however, the results have been confined to the reduction of simple prochiral ketones, and enzymes introduce only one asymmetric carbon at the reaction center of the substrate [1]. Development of the method to introduce more than one chiral center in one stage of the reaction is of great value for the manufacture of natural compounds having a number of chiral centers. Recently, we reported the isolation and characterization of four  $\beta$ -keto ester reductases from bakers' yeast [2-4]. One of them, named L-enzyme-1 (YKER-I, Yeast Keto Ester Reductase-I), has an excellent stereoselectivity in  $\beta$ -keto ester reduction. This enzyme preferentially utilizes NADPH as the coenzyme and reduces  $\beta$ -keto esters to give L(S)-hydroxy

esters exclusively [2,5].  $\alpha$ -Substituted  $\beta$ -keto esters are also reduced by this enzyme [3,5,6]. Since these compounds enolize and racemize easily in aqueous solutions, the substrate remains racemic throughout the reaction. The reduction of these compounds with L-enzyme-1 affords only one stereoisomer out of four possible stereoisomers in high yield [3,5,6].

This report will describe a new system of asymmetric synthesis; asymmetric reduction accompanied by simultaneous kinetic resolution of dynamic and static optically active centers [7]. Dynamic optically active center is defined as an optically active center, the configuration of which is mobile due to certain reason such as enolization, non-stereoselective exchange, pseudo-rotation, and so on. Static optically active center is configurationally rigid optically active center. The purpose of this method is introduction of three chiral centers in one stage of the reaction. We chose asymmetric reduction of  $\alpha$ -alkyl- $\beta$ -keto ester of secondary alcohol, **1**, as a typical

## BIOORGANIC CHEMISTRY — Bioorganic Reaction Theory —

### Scope of research

Biochemical reactions are studied from the viewpoint of physical organic chemistry. Namely, the reaction mechanism and stereochemistry of NAD-dependent oxidoreductases are explored. Stereospecific redox transformations mediated by certain biocatalysts such as microbes, enzymes, cultured tissues are also studied. The results will be applied to develop new organic reactions.



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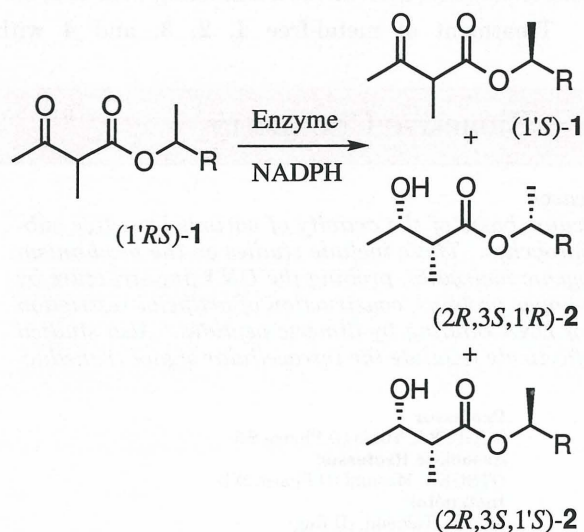
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example for this system. Microbial reduction of  $\beta$ -keto esters of secondary alcohols with unsatisfactory stereoselectivity has been reported [8].

Various keto esters, **1**, were subjected to the reduction by L-enzyme-1 and the results are summarized in Table 1. The reduction of keto ester **1** with L-enzyme-1 preferentially affords the (2*R*,3*S*,1'*R*)-hydroxy ester **2** in moderate to high diastereoselectivity. The reduced product was composed of two stereoisomers only, (2*R*,3*S*,1'*R*) and (2*R*,3*S*,1'*S*), in each case; no other six possible stereoisomers were detected. Thus, the enantiomeric excesses in the products are quantitative. The diastereoselectivity of this enzyme depends on the structure of alkoxy moiety. Steric bulk of the substituent plays an important part of the substrate recognition of this enzyme. Reduction of keto ester of acyclic aliphatic alcohol, **1a**, affords the corresponding hydroxy ester in low diastereoselectivity. Introduction of cyclic substituent such as phenyl or cyclohexyl, **1b** or **1k**, increases the diastereoselectivity. Further modification of the phenyl ring, **1c** - **1g**, however, does not alter the diastereoselectivity. A remarkable change in the diastereoselectivity can be seen in the esters having heteroatom(s) in the ring such as pyridyl or dithianyl, **1h** - **1j** and **1l**. Particularly, the reduction of dithianylethyl ester affords the (2*R*,3*S*,1'*R*)-hydroxy ester in more than 95 % purity out of possible eight stereoisomers. Starting from racemic compounds, this enzyme can produce hydroxy esters with three chiral centers in high stereoselectivity.



Scheme 1

In conclusion, introduction of three chiral centers in one stage of the reaction from racemic compounds was realized. The enzyme can recognize plural chiral centers to produce useful chiral building blocks containing plural asymmetric carbons.

Table 1. Stereoselectivity of Optical Resolution

	R	Yield %	d.e. <sup>a</sup> %	E <sup>b</sup>
a	Hex	33.9	65.6	6.5
b	Ph	44.6	73.6	13.3
c	2-Cl-Ph	34.6	69.7	8.2
d	2-Me-Ph	48.8	74.6	14.6
e	4-Cl-Ph	29.0	76.7	10.7
f	4-Me-Ph	39.6	74.6	12.2
g	4-NO <sub>2</sub> -Ph	36.1	80.4	15.9
h	2-Py	38.2	79.7	15.9
i	3-Py	43.0	86.3	29.0
j	4-Py	35.5	91.2	35.8
k	Cyclohexyl	34.5	77.6	12.2
l	1,3-Dithianyl	43.6	90.6	41.4

a: Ratio of (2*R*, 3*S*, 1'*R*) to (2*R*, 3*S*, 1'*S*).

b:  $E = [\text{Log}((1-ee(S))/(ee(S)+ee(P))) \times (1-ee(S))]/$   
 $[\text{Log}((1-ee(S))/(ee(S)+ee(P))) \times (1+ee(S))].$

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# Novel Zinc Chelators Which Inhibit the Binding of HIV-EP1, a Zinc Finger Protein, to NF- $\kappa$ B Recognition Sequence

Masami Otsuka, Mikako Fujita, and Yukio Sugiura

In order to manipulate the function of zinc finger proteins, several zinc-binding molecules comprising dimethylaminopyridine and histidine units have been prepared. NMR study showed that trityl and carboxyl groups contributed to increase zinc-binding capability of the chelators. These molecules exhibited remarkable inhibitory effect on the DNA binding of the human immunodeficiency virus type 1 enhancer binding protein HIV-EP1 which contains two C<sub>2</sub>H<sub>2</sub> type zinc fingers. DNA-binding capability of HIV-EP1 was recovered by adding extra zinc, confirming the inhibition to be caused by the removal of zinc from HIV-EP1. This approach could be a novel strategy for the control and elucidation of biochemical processes.

**Keywords:** HIV-EP1 / Zinc Finger / Transcription factor / DNA-binding

Zinc finger proteins constitute a major group of transcription factor and play important roles in the gene expression. Our interest has been focused on a C<sub>2</sub>H<sub>2</sub> type zinc finger protein HIV-EP1 which binds to DNA  $\kappa$ B site (5'-GGGACTTTC-3') present in the long terminal repeat of HIV provirus to activate the HIV-1 gene expression. It was thought that the function of this zinc protein could be modulated by ejecting the zinc and inhibition of HIV-EP1 would lead to the interference of the replication of AIDS virus. The objective of this study is to construct an efficient zinc-coordinating system which can abstract zinc from

HIV-EP1 to inhibit DNA binding.

Previously we reported a metal-chelating system comprising a dimethylaminopyridine and histidine methyl ester **1** (1). We considered that the structure of the compound **1** could be modified so as to be an efficient zinc trapper. First we tried to introduce a trityl group into the imidazole in order to alter the chelating characteristics of the imidazolyl group. We also attempted to change the methyl ester groups of compound **1** into carboxyls. Thus, we prepared trityl and/or carboxyl derivatives **2-4** starting with **1** (2, 3).

Treatment of metal-free **1**, **2**, **3**, and **4** with

## BIOORGANIC CHEMISTRY — Bioactive Chemistry —

### Scope of research

*The major goal of our laboratory is to elucidate the molecular basis of the activity of various bioactive substances by biochemical, physicochemical, and synthetic approaches. These include studies on the mechanism of sequence-specific DNA cleavage by antitumor or carcinogenic molecules, probing the DNA fine structure by various chemicals, studies on the DNA recognition of zinc-finger proteins, construction of artificial restriction enzyme, and model study on the cooperative mechanism of DNA binding by dimeric peptides. Also studied are the design and synthesis of functional molecules that effectively regulate the intracellular signal transduction or that applicable to fluorescence detection of DNA.*



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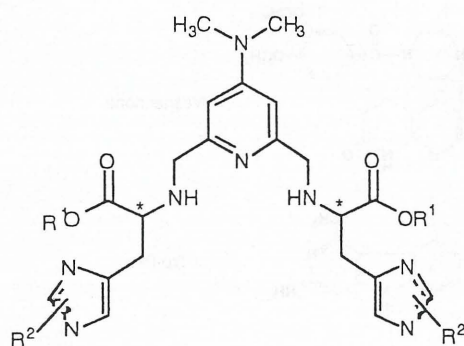
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equimolar  $\text{ZnSO}_4$  in MeOH afforded the corresponding 1:1 zinc complexes. Zinc-chelated **1**, **2**, **3**, and **4** thus formed were distinguished from the metal-free **1**, **2**, **3**, and **4** by  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectroscopy. The zinc-binding affinity of the synthetic ligands **2**, **3**, and **4** was compared with that of ligand **1** by competitive zinc binding experiments using  $^1\text{H}$  NMR. The affinity of the ligand **1** for zinc was decreased by introducing trityl group. However, zinc binding power was greatly improved by changing the methyl ester to the carboxyl, and *RS*-isomer **4** showed the highest affinity for zinc.



Compound	R <sup>1</sup>	R <sup>2</sup>	Stereochemistry (*)
<b>1</b>	CH <sub>3</sub>	H	<i>SS</i>
<b>2</b>	CH <sub>3</sub>	Trt	<i>SS</i>
<b>3</b>	H	Trt	<i>SS</i>
<b>4</b>	H	Trt	<i>RS</i>

The synthetic chelators **1-4** were found to exhibit remarkable inhibitory effect on the DNA binding of HIV-EP1, even more potent than that of EDTA, as demonstrated by electrophoretic mobility shift assay. The most potent was compound **1** which inhibited the DNA binding almost completely at 0.4 mM concentration. The most strong zinc chelator **4** showed somewhat weaker inhibition. Discrepancy between the DNA-binding inhibitory effect and the zinc-binding power of ligands may be due to their relatively low solubility in aqueous media or possibly due to the dif-

ference in the dissociation of the carboxyl group of the ligand depending on the solvent constitution ( $\text{CD}_3\text{OD}-\text{D}_2\text{O}$  (4:1) for the NMR measurement and  $\text{H}_2\text{O}-\text{CH}_3\text{OH}$  (96:4) for the DNA-binding experiments). All these ligands were shown to be stronger inhibitors of DNA binding compared with EDTA although EDTA showed stronger affinity for zinc, suggesting the superiority of the nitrogen-containing heterocyclic structure in terms of amino acid interaction, hydrophobic interaction, or possibly electronic effect favourable for the formation of presumed intermediary ternary complex with HIV-EP1-Zn. When zinc was introduced during or after the DNA-binding inhibition reaction with compound **1** (0.7mM), total recovery of HIV-EP1-DNA complex was observed. Ethidium displacement and footprinting experiments indicated that **1** has virtually no interaction with DNA. These indicated that the inhibition was indeed caused by the removal of zinc from the zinc finger moiety of HIV-EP1 and ruled out a competition between ligand **1** and HIV-EP1 for binding to DNA.

Thus, we developed novel zinc-binding heterocycles and succeeded in the inhibition of DNA binding of a zinc finger protein HIV-EP1. Since this approach can basically be applicable to any zinc proteins and the further structural modification of the pyridine-histidine system could be easily attained, the present study may provide a basis for the control and elucidation of various biochemical processes.

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## Cell Differentiation Induced by Poly(ADP-ribose) Synthetase Inhibitors

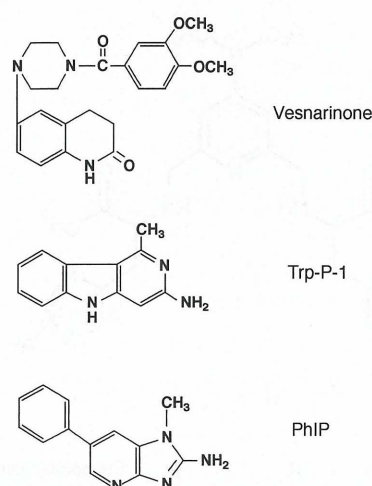
Kunihiro Ueda, Marek Banasik, Sachiko Nakajima, Hye-Young Yook and Takahiro Kido

We recently found two groups of inhibitors of poly(ADP-ribose) synthetase, *i.e.* vesnarinones and heterocyclic amines, to induce differentiation of murine teratocarcinoma EC cells in culture. Cell morphology changed almost completely in 5 to 7 days after treatment with 70  $\mu$ M benzylvesnarinone or 1 mM PhIP. Analyses of poly(ADP-ribose) synthesis and NAD concentrations in EC cells suggested that poly(ADP-ribose) might play a role in initiation of cell differentiation.

**Keywords:** Teratocarcinoma / NAD / Vesnarinone / Heterocyclic amines / Automodification

Poly(ADP-ribose) is a macromolecule synthesized from NAD in nuclei of eucaryotic cells (1). After 30 years from its discovery, precise biological functions of poly(ADP-ribose) remain still unclear. In order to obtain useful tools for *in vivo* studies, we made an extensive survey of poly(ADP-ribose) synthetase inhibitors for years, and found a number of potent inhibitors (2). Recently we added several more to the list of inhibitors, among which were vesnarinones and heterocyclic amines [3]. In this report, we present evidence that these new inhibitors are capable of inducing cell differentiation and that poly(ADP-ribose) plays a role in this cellular event.

Vesnarinone (Fig. 1) is a therapeutic drug used for cardiac failure. Its action is reportedly to increase the intracellular  $\text{Ca}^{2+}$  concentration [4]. We found this compound to inhibit the activity of poly(ADP-ribose) synthetase. The inhibition was not very strong; 14 and 32% inhibition was observed at 0.1 and 0.5 mM, respectively. Other derivatives were less potent.



**Figure 1.** Chemical structures of vesnarinone (3,4-dihydro-6[4-(3,4-dimethoxybenzoyl)-1-piperazinyl]-2(1H)-quinolinone), Trp-P-1 (3-amino-1,4-dimethyl-5H-pyrido[4,3-b]indole), and PhIP (2-amino-1-methyl-6-phenylimidazo[4,5-b]pyridine).

### BIOORGANIC CHEMISTRY — Molecular Clinical Chemistry —

#### Scope of research

*This laboratory was founded in 1994, aiming at the linkage between basic sciences and clinical medicine. Thus, our research scope encompasses structures/functions of various biomolecules, their abnormalities causing diseases, and their molecular mechanisms of control useful to therapy. Our current interest is focussed on pathophysiological roles of poly(ADP-ribose) in carcinogenesis and apoptosis, and of A/ $\beta$ -amyloid precursor proteins in Alzheimer's disease. Gene technology and its application to clinical diagnosis are another target of our current effort.*



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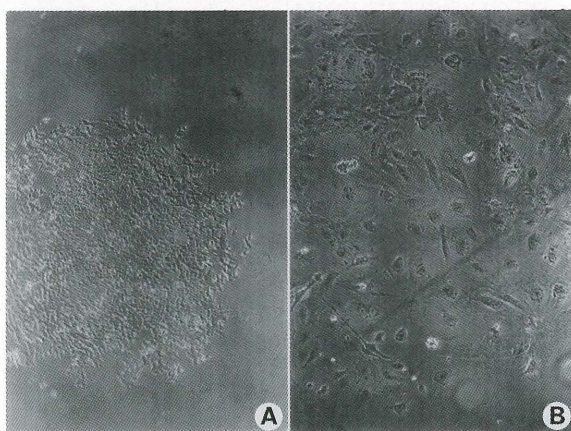


Among heterocyclic amines or pyrolysis products of various amino acids, Trp-P-1 and Trp-P-2 are the most potent in mutagenesis and/or carcinogenesis [5]. We found these  $\gamma$ -carbolines to inhibit the poly(ADP-ribose) synthetase activity. Trp-P-1 was a strong inhibitor ( $IC_{50} = 0.22$  mM), while Trp-P-2 was a weak inhibitor ( $IC_{50} = 2.2$  mM). In addition to Trp-P-1 and Trp-P-2, many other heterocyclic amines, including PhIP that is the most abundant in foods, proved to be, more or less, inhibitory to poly(ADP-ribose) synthetase (6).

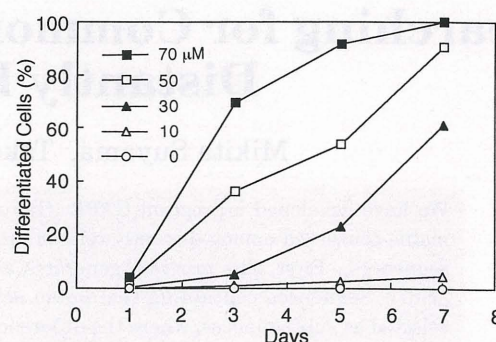
We recently found that vesnarinones and heterocyclic amines are also capable of inducing differentiation of murine teratocarcinoma EC cells. EC cells are pluripotent stem cells and differentiate into many cell types when treated with inducers, including inhibitors of poly(ADP-ribose) synthetase [1, 6].

The EC cells grew in small-cell mass, free of contact inhibition, in control culture. When the cells were cultured for a day or longer in the presence of vesnarinone, benzylvesnarinone, Trp-P-1, or PhIP, the cell mass dispersed, and each cell became larger, flatter and contact-inhibited (Fig. 2). Studies with varying concentrations of benzylvesnarinone (Fig. 3) showed that the cells started to change morphology from the second day, and almost all cells treated with  $>50$   $\mu$ M of the drug acquired the differentiated cell shape in a week.

We then analyzed acceptors and extents of poly(ADP-ribose) synthesis in the course of EC cell differentiation. Our preliminary data indicated that the intracellular NAD concentration decreased precipitously within a day after treatment with an inducer of differentiation (e.g. all-*trans*-retinoic acid), and, at the same time, endogenous poly(ADP-ribose) synthesis on various proteins including the synthetase itself increased remarkably, whereas the synthetase activity, as assayed *in vitro*, continued to decrease throughout the course (6). The transient activation of the synthetase automodification at an early stage of differentiation appeared to be relevant to massive DNA fragmentation and apoptosis induced by the differentiation inducer.



**Figure 2.** Phase-contrast photomicrographs of murine teratocarcinoma EC cells cultured (A) with no addition for 5 days or (B) with 1 mM PhIP for 7 days (6).



**Figure 3.** Time course of EC cell differentiation induced by varying concentrations of benzylvesnarinone (6).

These results, together with our previous observations with other inhibitors of poly(ADP-ribose) synthetase, such as 3-aminobenzamide [7] or 4-hydroxyquinazoline [6], support the view that induction of teratocarcinoma cell differentiation is a property common to inhibitors of this enzyme. Thus, poly(ADP-ribose) appears to participate in cell differentiation at an early stage of induction.

In addition to EC cells, other malignant cells, including Friend erythroleukemia cells and HL-60 promyelocytic leukemia cells, have been shown to be induced to differentiate by poly(ADP-ribose) synthetase inhibitors. These results may suggest a novel way of chemotherapy, that is, normalizing malignant cells by induction of differentiation.

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# Searching for Common Sequence Patterns among Distantly Related Proteins

Mikita Suyama, Takaaki Nishioka, and Jun'ichi Oda

We have developed a program GAPE (Gap Allowing Pattern Explorer) to extract amino acid sequence motifs conserved among distantly related proteins. The GAPE program is designed to allow gaps in the sequences. First, this program generates all possible amino acid patterns composed of up to 5 amino acids. Sequences containing the amino acid residues in the same order to a generated pattern are selected as subsequences, where the differences in the distances between two consecutive amino acids are neglected. Then, the motifs are extracted from the subsequences under the conditions where the all four distances between the five amino acids are fixed. In this stage, motifs with gaps in the subsequence are also found by relaxing one of the four fixed distances. Statistical significance for a motif obtained is calculated based on the amino acid composition of the sequences under consideration. When the GAPE program is applied to 64 ATP-(AMP-forming)-related sequences, motifs extracted with low expectation of occurrence contain some of the amino acid residues chemically proved to be involved in the ligand recognition.

**Keywords:** amino acid sequence / motif / statistical significance / molecular evolution / enzyme reactions / database / WWW

There are many short sequence patterns, often called motifs, among distantly related proteins. These motifs have been derived from a common ancestor and often directly correspond to the functionally important sites, because of the resistance against the mutation on the sites. Then the motifs facilitate to detect very distant relationships that have been obliterated in whole amino acid sequences. Such patterns are useful for the prediction of protein function of uncharacterized sequences such as those determined by genome sequencing projects. As the number of amino acid sequences determined has rapidly increased, it has become clear that automated procedures to find motifs would be useful.

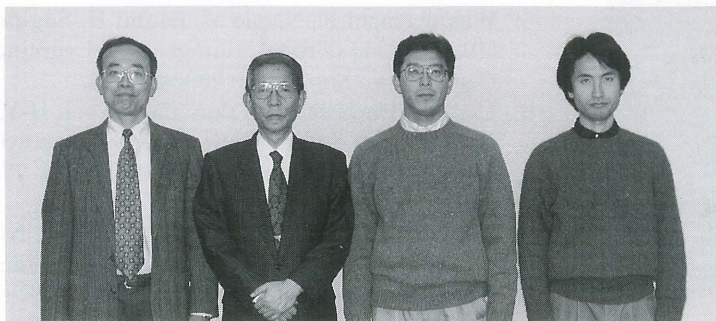
Two methods have been applied to discover sequence motifs, alignment method and pattern-generating method. The first method has such disadvantage that it is hard to make multiple sequence alignment unless the sequences have global similarities. The second method intended for automated search, generates all 3-amino acid patterns including intervening residues of fixed length. Motifs with conservative substitutions are identified on the bases of amino acid patterns common to a majority of the sequences.

About one-tenth of the motifs found in protein sequences, however, contain intervening residues of flexible length called "gap". Any methods so far developed do not explicitly deal with gaps in local

## MOLECULAR BIOFUNCTION — Functional Molecular Conversion —

### Scope of research

*Our research aims are to analyze structure-function relationships of biocatalysts in combination with organic chemistry, structural biology and computer science, and to apply biocatalysts to stereospecific organic synthesis. Major subjects are the design and preparation of monoclonal antibodies catalyzing chemiluminescence, the reaction mechanisms of glutathione synthetase from *E. coli* with static, cryogenic, and time-resolved X-ray crystallography, the mechanism of action of lipase-activating protein, crystallographic analysis of asparagine synthetase and  $\gamma$ -L-glutamyl-L-cystein synthetase, and molecular evolution of enzymes and metabolic pathways*



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patterns because of combinatorial problems.

We have developed a motif search algorithm GAPE which explicitly deals with gaps in the sequences [1]. GAPE does not compare the sequences each other to find common patterns, but generate all possible patterns to screen out the subsequences. Initially, all possible 3-amino acid patterns (8,000 patterns) are generated. For each pattern, subsequences of length  $\leq W_{\max}$  that match with a pattern in the order of the three amino acids are searched, and if  $\geq s_{\min}$  subsequences are detected, they are stored in an array together with the pattern. These 3-amino acid order patterns selected by the above procedure are then added with one more amino acid residue to find 4-amino acid order patterns. The 4-amino acid order patterns satisfying the above criteria of  $s_{\min}$  and  $W_{\max}$  are subjected to next extension of the patterns. This procedure is repeated up to 5-amino acid order patterns. In the next step, the subsequences having the same 5-amino acid order pattern are compared with each other with respect to the four distances,  $d_1$ ,  $d_2$ ,  $d_3$ , and  $d_4$ , between the five amino acids. When all the corresponding distances are equivalent in  $\geq s_{\min}$  subsequences, the pattern with the distances is accepted as a rigid motif. Flexible motif which has gaps in subsequences is obtained by relaxing one of the four distances.

GAPE was applied to extract flexible motifs in the sequences of ATP-(AMP-forming)-related enzymes which use ATP as a substrate and form AMP as a product. Their amino acid sequences were systematically collected on the database LIGAND (Ligand Chemical Database for Enzyme Reactions) [2], in which 157 sequences of 37 enzymes were registered. After removing the closely related sequences, 64 sequences were left as the representative sequences.

Under the search condition of  $W_{\max} = 20$ ,  $s_{\min} = 3$  and  $r_{\max} = 3$ , 308 rigid and 287 flexible motifs were obtained with an expected value of occurrence of a motif less than 5 % ( $E < 0.05$ ). The motif with the lowest  $E$  value was K-M-S-(x1)-S-(x2)-N, which occur in the sequences of 7 aminoacyl-tRNA synthetases class I. Tetrapeptide H-I-G-H, which is known to be conserved among aminoacyl-tRNA synthetases class I, was also found as a flexible motif P-(x1)-A-(x3,4)-H-(x1)-G-H. In the three-dimensional structure of tyrosine-tRNA ligase, this region has been shown to be a part of the adenylate binding site (Brick et al., 1989). Most of the motifs obtained are variations of these two motifs. All of the sequences of aminoacyl-tRNA synthetases class I contain some of the variations of the two motifs.

One of the flexible motifs found among aminoacyl-tRNA synthetases class II is G-(x2)-P-(x2,3)-G-(x3)-G-(x2)-R (Figure 1). The enzymes containing this motif are lysine-tRNA ligase (EC 6.1.1.6), aspartate-tRNA ligase (EC 6.1.1.12), asparagine-tRNA ligase (EC 6.1.1.22), and aspartate-ammonia ligase (EC 6.3.1.1). This is the only motif with  $E < 0.05$  that occurs in the sequence of aspartate-ammonia ligase. The similarity of aspartate-ammonia ligase to

S17011	CNALEY	GLPP-TGGWCGGIDR	LAMFL
SYRTDT	IDSFRF	GAPPH-AGGGIGLER	VTMLF
S23761	LDALKY	GTPPH-AGLAFGLDR	LTMLL
SYBYDM	LNAFDM	GTPPH-AGFAIGFDR	MCAMI
SYECNT	RDLRRY	GTVPH-SGFGLGFER	LIAYV
AJECNA	HQALLR	GEMPQTIGGGIGQSR	LTMLL
Motif		G P G G R	

**Figure 1.** Motifs extracted from ATP-(AMP-forming)-related sequences. The first column represents PIR entry codes for each sequence. Enzyme and the residue number of the first amino acid in the motif are as follows: S17011 = lysine-tRNA ligase, 543; SYRTDT = aspartate-tRNA ligase, 462; S23761 = aspartate-tRNA ligase, 143; SYBYDM = aspartate-tRNA ligase, 594; SYECNT = asparagine-tRNA ligase, 427; AJECNA = aspartate-ammonia ligase, 285.

aminoacyl-tRNA synthetases class II was first reported by Gatti and Tzagoloff (1991). For aspartate-ammonia ligase from *Escherichia coli*, mutation of the arginine residue in the motif confirmed that the residue is crucial for its activity (Hinchman et al., 1992). This motif provides another support for the possibility that these two enzymes evolved from a common ancestral enzyme.

The motifs obtained among the ligand-related sequences by GAPE are well correlated with the ligand and recognition sites of the sequences. These motifs imply that the enzymes sharing the motifs have been evolved from a common ancestor recognizing the ligand, though none of global sequence similarity is detected. The ancestral enzymes would have been diverged to specific reactions for each enzyme retaining the ligand specificity.

Amino acid sequences for the motif search have to be classified and systematically collected according to protein function such as ligand specificity or reaction type. For this purpose, we have constructed LIGAND. It is actually composed of two databases; ENZYME and COMPOUND. ENZYME contains the EC numbers, names, chemical equations catalyzed, substrates, products, cofactors, inhibitors of 3,489 enzymes. COMPOUND, a database of 5,118 chemical substances appeared in ENZYME, contains their chemical names, chemical structures (in a connection table format and in an image), and CAS registry number. ENZYME has a link to the databases of DNA base sequences, amino acid sequences, 3-D structures, and inheritance diseases and has a link to metabolic pathways. Each chemical substance in the COMPOUND has a link to ENZYME which enables to collect a set of enzymes and their sequences related to a substance desired. The WWW version of LIGAND is served on GenomeNet (<http://www.genome.ad.jp>).

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# Identification of Asp10 as the Active Site Nucleophile of L-2-Haloacid Dehalogenase of *Pseudomonas* sp. YL

Kenji Soda, Nobuyoshi Esaki, Tatsuo Kurihara and Ji-Quan Liu

L-2-Haloacid dehalogenase (EC class: 3.8.1.2) catalyzes the hydrolytic dehalogenation of L-2-haloalkanoic acids to produce the corresponding D-2-hydroxyalkanoic acids. We have analyzed the reaction mechanism of the enzyme from *Pseudomonas* sp. YL by means of  $^{18}\text{O}$  incorporation experiment and tandem mass spectrometrical analysis of the labeled enzyme, and found that Asp10 is the active site nucleophile. Asp10 probably attacks the  $\alpha$ -carbon of the substrate leading to the formation of an ester intermediate, which is hydrolyzed by nucleophilic attack of a water molecule on the carbonyl carbon atom.

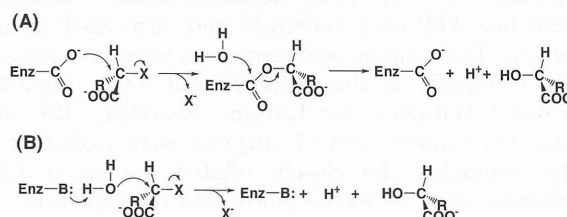
**Keywords:** Dehalogenation / Haloalkanoic acid / Ionspray mass spectrometry

L-2-Haloacid dehalogenase (L-DEX) catalyzes the hydrolytic dehalogenation of L-2-haloalkanoic acids with inversion of the  $\text{C}_2$ -configuration producing the corresponding D-2-hydroxyalkanoic acids. We have isolated and purified thermostable L-2-haloacid dehalogenase (L-DEX YL) from a 2-chloroacrylate-utilizable bacterium, *Pseudomonas* sp. YL (1), cloned its gene (2), and constructed the overexpression system (3). The enzyme is composed of 232 amino acid residues (2), and its amino acid sequence is highly similar to those of L-DEXs from other bacterial strains and haloacetate dehalogenase H-2 from *Moraxella* sp. strain B (2).

Two different mechanisms have been proposed for the reactions of L-DEXs (Fig. 1) (4). According to the mechanism shown in Fig.1A, a carboxylate group of Asp or Glu acts as a nucleophile to attack the  $\alpha$ -carbon of L-2-haloalkanoic acid, leading to the formation of an ester intermediate. This is hydrolyzed by an attack of water molecule activated by a basic amino acid residue of the enzyme. Alternatively, water is

activated by a catalytic base of the enzyme, and directly attacks the  $\alpha$ -carbon of L-2-haloalkanoic acid to displace the halogen atom (Fig.1B).

We conducted single- and multiple-turnover enzyme reactions in  $\text{H}_2^{18}\text{O}$  in order to examine the adequacy for these two mechanisms. The single-turnover reaction was carried out in the solution containing the enzyme in excess of substrate, whereas the multiple-turnover reaction was done by using an excess amount of substrate. If the reaction proceeds through the Fig.1B mechanism,  $^{18}\text{O}$  is incorporated into the product both in single- and multiple-turnover



**Figure 1.** Proposed mechanisms of L-DEX.

## BIOFUNCTIONAL MOLECULES — Molecular Microbial Science —

### Scope of research

Structure and function of biocatalysts, in particular, pyridoxal enzymes, NAD enzymes, and enzymes acting on xenobiotic compounds are studied to elucidate the dynamic aspects of the fine mechanism for their catalysis in the light of recent advances in gene technology, protein engineering and crystallography. In addition, the metabolism and biofunction of selenium and some other trace elements are investigated. Development and application of new biomolecular functions of microorganisms are also studied to open the door to new fields of biotechnology. For example, molecular structures and functions of thermostable enzymes and their application are under investigation.



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reactions. In the case of the Fig.1A mechanism, the single-turnover reaction causes  $^{18}\text{O}$ -incorporation into the carboxylate group of the enzyme, but not into the product. In the multiple-turnover reaction, both the product and the carboxylate group of the catalytic residue are labeled with  $^{18}\text{O}$ .

Under the single-turnover conditions, we found that less than 10% D-lactate produced in  $\text{H}_2^{18}\text{O}$  contained  $^{18}\text{O}$ , whereas under the multiple-turnover conditions, more than 95% D-lactate contained  $^{18}\text{O}$ . These suggest that an oxygen atom of water molecule is first transferred to the enzyme, and then to the product. This supports the mechanism involving an ester intermediate shown in Fig.1A, but does not the Fig.1B mechanism, in which an oxygen atom of solvent water is directly transferred to the product.

To identify the position of the incorporated  $^{18}\text{O}$  in the enzyme, a mutant enzyme L-DEX T15 was constructed by introducing three lysyl residues at the positions of 11, 176 and 185 of L-DEX YL by site-directed mutagenesis. Properties of the mutant L-DEX T15 such as specific activity toward L-2-chloropropionate and optimum pH were identical to those of the wild-type enzyme.

L-DEX T15 was used to carry out a multiple-turnover reaction in  $\text{H}_2^{18}\text{O}$  with L-2-chloropropionate as a substrate. After completion of the reaction, the enzyme was digested with lysyl endopeptidase, and the resulting peptide fragments were separated on a capillary column interfaced with an ionspray mass spectrometer as a detector (PE-Sciex API III). When the spectrometer was in the single-quadrupole mode, the total ion current chromatogram displayed several peaks. The molecular mass of peptide 6-11 was 654.5 Da, which is approximately 4 Da higher than the predicted molecular mass (650.75 Da), although the amino acid sequence of this peptide was Gly-Ile-Ala-Phe-Asp-Lys, which is identical to that predicted from nucleotide sequence. Molecular masses of all other peptides were indistinguishable from the predicted ones. These results indicate that two  $^{18}\text{O}$  atoms were incorporated solely into the peptide 6-11, which contains Asp10.

L-DEX T15 was incubated in  $\text{H}_2^{18}\text{O}$  with or without L-2-chloropropionate under the multiple-turnover conditions. The enzyme was digested with lysyl endopeptidase, and the peptide 6-11 containing Asp10 was isolated with a reverse phase HPLC column. Two atoms of  $^{18}\text{O}$  were incorporated into this peptide when L-DEX T15 was incubated in  $\text{H}_2^{18}\text{O}$  in the presence of L-2-chloropropionate. However,  $^{18}\text{O}$  was not incorporated when the enzyme was incubated in the absence of L-2-chloropropionate.

To identify the position of the incorporated  $^{18}\text{O}$  more precisely, the peptide 6-11 was subjected to tandem MS/MS spectrometrical analysis. Fragmentations of the peptides were performed using mass spectrometer in the daughter ion scan mode. The parent ions of  $m/z$  654.5 and  $m/z$  650.2, corresponding to  $^{18}\text{O}$ -labeled and unlabeled hexapeptides, respectively, were selected in the first quadrupole, and subjected to collision-induced fragmentation in a

collision cell in the second quadrupole. The Y' series daughter ions at  $m/z$  484.0, 413.1, and 266.0 derived from  $^{18}\text{O}$ -labeled peptide correspond to the fragments of Ala-Phe-Asp-Lys, Phe-Asp-Lys, and Asp-Lys, respectively. They are about 4 Da higher than those of ions at  $m/z$  480.3, 409.1, and 262.0 of the unlabeled peptide. However, after the deletion of Asp, molecular masses of the remaining portions (Lys) of these two peptides were closely similar to each other (146.8). These results suggest that two atoms of  $^{18}\text{O}$  of solvent water are incorporated into Asp10 of the enzyme during the dehalogenation reaction.

Accordingly, the dehalogenation reaction of L-DEX probably proceeds through the ester intermediate mechanism in which Asp10 functions as a nucleophile (Fig.1A). Since two  $^{18}\text{O}$  atoms were incorporated into Asp10, both two oxygen atoms of the carboxylate group of Asp10 are equivalent and either can attack the substrate. The replacement of Asp10 by another amino acid residue causes significant loss in the enzyme activity (5). This also supports the involvement of Asp10 in the catalysis.

The same reaction mechanism in which a nucleophilic carboxylate group takes part has been proposed for three types of hydrolases: rat liver microsomal epoxide hydrolase (6), haloalkane dehalogenase from *Xanthobacter autotrophicus* GJ10 (7), and (4-chlorobenzoyl)coenzyme A dehalogenase from *Pseudomonas* sp. strain CBS3 (8). Epoxide hydrolase and haloalkane dehalogenase are structurally related to each other, but (4-chlorobenzoyl)coenzyme A dehalogenase does not share sequence identity with either of these two enzymes. L-DEX does not show a significant sequence similarity to any of these three enzymes. Hence, L-DEX resembles these hydrolases solely by the presence of an active site nucleophilic carboxylate.

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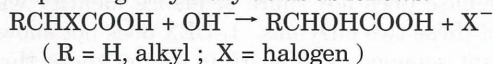
# Structure-Function of Haloacid Dehalogenase: Tertiary Structure Elucidated by X-Ray Crystallographic Study

Yasuo Hata, Tomomi Fujii, and Tamao Hisano

The structure of the dimeric L-2-haloacid dehalogenase from *Pseudomonas* sp. YL was determined at 2.5 Å resolution by X-ray crystallographic studies. The structure of the enzyme subunit consists of two domains: a core-domain and a sub-domain. The core-domain has an  $\alpha/\beta$  structure where a six-stranded parallel  $\beta$ -sheet is flanked with five  $\alpha$ -helices. The sub-domain has four  $\alpha$ -helices, and is inserted between the first  $\beta$ -strand and  $\alpha$ -helix of the core-domain. Several residues which were suggested to be involved in the catalysis by mutagenesis studies, including the nucleophilic residue Asp10, are found to be clustered at the bottom of the cleft encompassed by the two domains. This implies that the site around Asp10 in the cleft may be the reasonable active site. The hydrophilic environment around the active site is convenient for the enzyme to bind haloacids, substrates possessing hydrophilic carboxyl groups.

**Keywords:** Dehalogenation/ Hydrolase/ X-ray structure / Catalytic mechanism

Halogenated organic compounds are widely used as materials for various industrial products such as insecticides and solvents, and cause serious environmental problems owing to their persistence and/or toxicity. Several kinds of bacteria have been found to be able to take up some of such compounds as sole carbon sources and to degrade them using enzymes called dehalogenases. 2-Haloacid dehalogenases (E.C. 3.8.1.2) isolated from several bacteria catalyze the hydrolytic degradation of 2-haloacids to produce the corresponding 2-hydroxy acids as follows:



The enzymes are classified into four types on the basis of the C<sub>2</sub> configurations of their substrates and reaction products.

L-2-Haloacid dehalogenase from *Pseudomonas* sp.

YL is a dimeric enzyme composed of two identical subunits each of which comprises 232 amino acid residues corresponding to the molecular weight of 26,179. It acts on L-2-haloalkanoic acids to yield D-2-hydroxyalkanoic acids. The catalytic mechanism of the enzyme has been studied by comprehensive site-directed mutagenesis (1) and <sup>18</sup>O incorporation (2). From the results of these studies, it has been proposed that Asp10 is the active site nucleophile attacking the C<sub>2</sub> atom of substrates.

In order to elucidate the catalytic and stereoselective reaction mechanisms of 2-haloacid dehalogenases, we have undertaken crystallographic studies of the enzymes. Recently, we succeeded in the structure determination of dimeric L-2-haloacid dehalogenase from *Pseudomonas* sp. YL at 2.5 Å resolution by double isomorphous replacement in X-ray crystallog-

## MOLECULAR BIOLOGY AND INFORMATION — Biopolymer Structure —

### Scope of research

Our research aims are to elucidate structure-function relationships of biological macromolecules, mainly proteins, by using physicochemical methods such as spectroscopic and X-ray diffraction methods. The following attempts have been mainly made in our laboratory for that purpose. (1) Peptide secondary or supersecondary structures in aqueous or hydrophobic environments are studied to get a principle of protein architecture, employing various spectroscopic methods. (2) X-ray diffraction studies on protein structures in crystal and in solution are carried out by crystallographic and/or small-angle X-ray scattering techniques to elucidate structure-function relationships of proteins.



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raphy.

Crystals of the enzyme were grown at 4°C by vapor diffusion, supplemented by repetitive seeding, against a 50 mM potassium dihydrogenphosphate solution (pH 4.5) containing 15% (w/v) polyethylene glycol 8000 and 1% (v/v) *n*-propanol. A typical crystal size was about 0.6 mm × 0.5 mm × 0.1 mm. The crystals belong to space group *C*2 with unit cell dimensions of  $a = 92.21 \text{ \AA}$ ,  $b = 62.78 \text{ \AA}$ ,  $c = 50.84 \text{ \AA}$  and  $\beta = 122.4^\circ$ , and contain two dehalogenase dimers in the unit cell. Assuming one subunit per asymmetric unit, the specific volume  $V_m$  results in  $2.37 \text{ \AA}^3/\text{Da}$ , which corresponds to a solvent content of 48.2%.

Uranyl and aurate derivative crystals were prepared at 25°C by soaking the native crystals in the solutions of 1 mM  $\text{UO}_2(\text{NO}_3)_2$  for 6 days and 3 mM  $\text{K}[\text{Au}(\text{CN})_2]$  for 4.5 days, respectively. They were isomorphous with native crystals. Diffraction data for the native and two derivative crystals were collected up to 2.5 Å resolution at 20°C on a Rigaku R-AXIS IIC imaging plate detector system using a graphite-monochromated  $\text{CuK}\alpha$  radiation produced by a fine-focused rotating anode X-ray generator Rigaku RU-300 operated at 40 kV-100 mA.

Difference Patterson maps of the derivatives, calculated at 5.0 Å resolution, showed an interpretable single major heavy-atom site for each derivative. The minor heavy-atom sites were located by difference Fourier maps. The refinement of heavy-atom parameters was carried out at 2.5 Å resolution using program package PHASES, and finally gave three U and two Au sites. In the final cycle of refinement, the anomalous scattering effects from the metals were considered for phase calculation. The mean figure of merit was 0.70 for the phase angles.

A 2.5 Å resolution electron density map calculated with multiple isomorphous replacement phases showed an obvious connectivity of electron density for the polypeptide chain. It was used for building a model of the enzyme structure on a graphics workstation using the program TURBO-FRODO. The N-terminal three residues and C-terminal ten residues were both invisible in the density map, and then excluded from the model. Consequently, the initial model for the subunit molecule comprised amino acid residues of 4 to 222.

The model consisting of 2,157 atoms in the protein and 19 water oxygens was refined with the simulated annealing protocol of the program X-PLOR. The crystallographic *R*-factor for the model was converged to 19.5% for 7,848 reflections ( $F \geq 2\sigma(F)$ ) within the resolution range of 8.0–2.5 Å. The r.m.s. deviations from ideal bond lengths and bond angles are 0.012 Å and  $1.8^\circ$ , respectively.

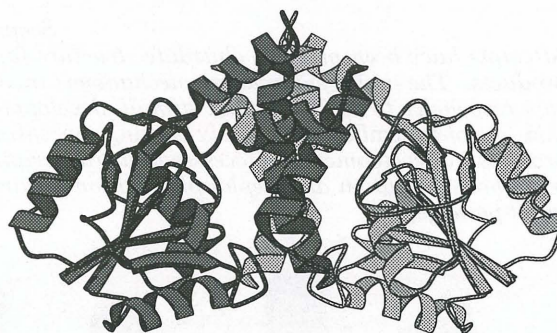
The subunit consists of two domains: a core-domain and a sub-domain. The core-domain has an  $\alpha/\beta$  type structure where a central six-stranded parallel  $\beta$ -sheet is flanked by three  $\alpha$ -helices on one side and two on the other. The domain is formed by amino acid residues 4 to 19 and 74 to 222. The sub-

domain consists of four  $\alpha$ -helices packed like a four-helix-bundle. The sub-domain is formed by amino acid residues 20 to 73, and is inserted between the first  $\beta$ -strand and the first  $\alpha$ -helix in the core-domain. There is a cleft formed between the two domains which are linked together by two-stranded antiparallel  $\beta$ -sheet.

The dimeric molecule has a compact ellipsoidal shape with dimensions of  $76 \text{ \AA} \times 40 \text{ \AA} \times 40 \text{ \AA}$  (Figure 1). The structure of the dimer is stabilized mainly by interactions among a cluster of hydrophobic residues from both subunits. Besides, polar residues, lining up across the molecular two-fold axis, form a linear hydrogen-bond network in the vicinity of the hydrophobic cluster. Almost all of these residues involved in the intersubunit interaction are highly conserved among L-2-haloacid dehalogenases.

The site-directed mutagenesis study has shown that mutation of the residue Asp10, Thr14, Arg41, Ser118, Lys151, Tyr157, Ser175, Asn177 or Asp180 in the subunit affects the activity of the enzyme. All the residues except for Arg41 belong to the core-domain, being located on the wall of the cleft between the two domains. The site occupied by these residues is positioned at the topological switch-point in the order of strands on the central  $\beta$ -sheet, and has enough room to accommodate a substrate. This suggests that the site can be the reasonable active site of the enzyme subunit. The active site cleft is widely open at its entrance, which is consistent with the observation that the enzyme can act on 2-haloacids including long alkyl groups. The environment around the catalytic site seems to be so hydrophilic that the enzyme can bind haloacids possessing the hydrophilic carboxyl group.

This project has been carried out in collaboration with the division of Molecular Biofunction - Molecular Microbial Science-, Institute for Chemical Research.



**Figure 1.** A dimeric molecule of L-2-haloacid dehalogenase from *Pseudomonas* sp. YL.

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## Regulation of *Arabidopsis thaliana* Flower Development

Koji Goto, Takashi Homma, Elliot M. Meyerowitz\* and Atsuhiko Oka

An *Arabidopsis thaliana* flower is composed of four organs, sepals, petals, stamens, and carpels. Development of these organs is determined by three classes of homeotic genes. One member gene *PISTILLATA* (*PI*) contributes to the formation of both petals and stamens. We have now cloned the *PI* gene with its promoter region and clarified the time and locations of *PI* expression during floral organogenesis of the wild type plant and the flower mutant plants (*pistillata*, *apetala3*, and *superman*).

**Keywords:** ABC model/Floral development/Homeotic gene/MADS box/Transcription factor

Occurrence of cell divisions in higher plants such as *Arabidopsis thaliana* is generally restricted to the meristems after embryogenesis has been finished. The apical meristem is organized tissues of pluripotent "stem" cells. Reproductive development in *Arabidopsis* is controlled by the activities of the inflorescence and the floral meristems derived from the apical meristem. The inflorescence meristem displays a pattern of indeterminate growth, whereas the floral meristem shows a determinate pattern of cell division and organogenesis, always resulting in the production of four whorls of floral organs (i.e., sepals, petals, stamens, and carpels). Genetic studies have shown that the establishment of the floral meristem requires several genes including *LEAFY* (*LFY*), *APETALA1* (*AP1*), and *APETALA2* (*AP2*), and that

the floral organogenesis is directed by three classes of organ identity genes (A, B, and C). The class A genes of *Arabidopsis* that are presently known are *AP1* and *AP2*, the class B genes are *PISTILLATA* (*PI*) and *APETALA3* (*AP3*), and the only known class C gene is *AGAMOUS* (*AG*). Representative mutant flowers defective in each class of the genes are shown in Figure (right half). How these homeotic genes specify the four whorls is interpreted by the ABC model in which the organs of each whorl are determined by combinations of the three class genes: sepals and carpels are directed by the class A and the class C genes, respectively; petals and stamens are given by a combination between the class A and B genes and between the class B and C genes, respectively; and the class A and C genes are mutually exclusive (see Figure) [1].

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To date, the molecular cloning of *PI*, *AG*, *AP1*, *AP2*, and *AP3* from *Arabidopsis* has been reported.

### MOLECULAR BIOLOGY AND INFORMATION — Molecular Biology —

#### Scope of research

Attempts have been made to elucidate structure-function relationships of genetic materials and various gene products. The major subjects are mechanisms involved in signal transduction and regulation of gene expression responsive to environmental stimuli, development of plant leaves and flowers, and plant-microbe interaction. As of December 1995, study is being concentrated on (1) roles of homeo domain proteins and MADS box proteins in developmental processes and transcriptional control in higher plants and (2) contribution of protein phosphorylation and dephosphorylation toward cell cycle control and signal transduction in plants and plant pathogens.



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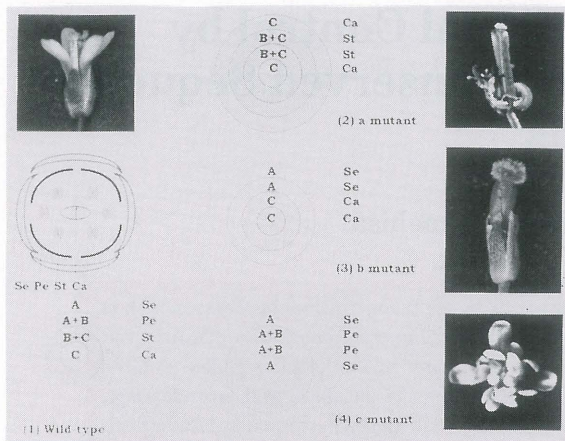
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**Figure.** Arrangement of floral organs in the wild-type *Arabidopsis* is shown in the left (1). Flowers in the right indicate those of a (2), b (3), and c (4) homeotic mutants, respectively. Four rings correspond to the whorls (Se, sepals; Pe, petals; St, stamens; and Ca, carpels), and A, B, and C within them indicate an expressing gene(s).

All of these gene products except *AP2*, and also their snapdragon homologs, *GLOBOSA* (*GLO*), *PLENA* (*PLE*), *SQUAMOSA* (*SQUA*), and *DEFICIENS* (*DEF*), respectively, have been characterized by a highly conserved 58-amino-acid DNA binding domain called MADS box. This name is come from yeast *MCM1* (minichromosome 1 maintenance), *Arabidopsis* *AG*, snapdragon *DEF*, and human *SRF* (serum response factor). *MCM1* and *SRF* are known to function as homodimers to regulate gene expression in response to extracellular signals. Since *PI* has been expected to be a member of the MADS box genes on the analogy of other organ identity genes, we have cloned it by using PCR-amplified *GLO* cDNA as a probe. A flower cDNA library was screened under the low stringency conditions. Eight positive clones obtained were all derived from the same RNA species [2]. Also a genomic clone corresponding to these cDNAs was isolated. The cloned DNA actually corresponds to the *PI* gene was confirmed by RFLP mapping and by sequencing of three *PI* mutant alleles (*pi-1*, *pi-2*, and *pi-3*). The *PI* cDNA has a single protein coding frame of 208-amino-acid residues. This protein includes a MADS box domain and a K box domain at the amino-terminal and the central portions, respectively. The latter domain seems to be liable to coiled-coil formation because of the resemblance to the amphipathic  $\alpha$ -helical region of keratin proteins [2].

To see the precise spatiotemporal expression pattern of *PI*, *in situ* hybridization was done with cross sections prepared from various developmental stages of flowers. Hybridization signals of *PI* mRNA appear at stage 3 flowers, the same stage when *AG* and *AP3* mRNA's are first detected. The signals are all located centripetally in a region of floral meristem, cells at which will later contribute the formation of not only the petal and stamen but also ovary. However, signals gradually become limited to the second and third

whorl cells, and remain at high levels until stages 10 and 11 where differentiation of the cells in each organ type is finished. This *PI* expression pattern is different from that of another class B gene *AP3*: signals of *AP3* mRNA are always restricted in the cells forming the second and third whorls and never detected in the center (fourth whorl) of developing flowers [2].

*PI* expression was analyzed in the *ap3-3* and *pi-1* mutant backgrounds. *PI* expression in *ap3-3* flowers is normal in early stages but not in later stages, suggesting a role for *AP3* in maintenance, but not establishment, of *PI* expression. *PI* mRNA in *pi-1* flowers seems to accumulate normally at stages 3-6, before the primordia of the second and third whorl organs begin to differentiate obviously, but then to decrease. The weaker mutant allele *pi-2* shows a less severe effect on the reduction of *PI* mRNA level. Thus, *PI* is likely to be necessary for maintaining its own expression [2]. This was confirmed by transient expression experiments in which the GUS reporter gene placed downstream of the *PI* promoter was introduced with a particle delivery procedure into the leaves of the wild-type plant and of a transgenic plant constitutively expressing *PI* [3]. The *superman* mutant displays the phenotype of reduction or elimination of the ovary, concomitant with appearance of many extra stamens in the forth whorl [1]. This phenotype is attributed to *PI* (and presumably *AP3*, too) expression at the forth whorl. Effects of overexpression of *PI* and *AP3* were tested with transgenic plants carrying the cauliflower mosaic virus 35S promoter-driven *PI* and *AP3* [3]. Plants overexpressing either gene are expected to show the normal phenotype, while those overexpressing both genes simultaneously are thought to convert homeotically sepal-to-petal and carpel-to-stamen, provided no other gene is required for the class B function. The latter gives the expected results, indicating *PI* and *AP3* being sufficient for the class B function. However, the former phenotype does not become normal: sepal-to-petal conversion occurs in the 35S::*PI* plants, whereas carpel-to-stamen conversion does in the 35S::*AP3* plants. These results suggest that *PI* induces *AP3* expression at the first whorl but not the forth whorl and that *AP3* induces *PI* expression at the forth whorl but not the first whorl. Although there is no direct biochemical evidence of *Arabidopsis* homeotic gene products being transcription factors at present, these experimental results suggest the existence of complicated regulatory network in control of flower morphogenesis. Assignment of DNA elements responsive to each factor on the *PI* promoter region is now in progress.

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# Prediction of Transcriptional Control by Promoter Specificity Index for Conserved Sequence Patterns

Wataru Fujibuchi and Minoru Kanehisa

We have developed a prediction method for expression specificities in the transcriptional process, which is known to be regulated in large part by promoter sequences, by observing the appearance of conserved sequence patterns in a group of promoters, such as for brain, liver, and house-keeping genes. Related promoters in the same group were compiled from EPD eukaryotic promoter database and an index (PSI, "Promoter Specificity Index") to represent the group specificity of each pattern was calculated. Each promoter was examined for its specificity to test the validity of these indices constructed from the rest of the promoters in our dataset. Currently, our system could discriminate 40 to 50 % of human promoters with 11 to 17 % of false positive rate.

**Keywords:** Transcriptional control/ Expression specificity/ Signal sequence/ Relative entropy/ Binomial distribution/ Markov chain/ Information content

Eukaryotic genes are expressed under complex regulatory systems that depend on time, place, and other environmental factors. Thus, detecting sequence differences of eukaryotic promoters in different tissues may provide clues to understanding mechanisms of eukaryotic gene expression. It is well known that the gene expression is highly regulated by the level of transcription initiation after the cooperative binding of transcription factors to signal pattern sequences. Experimental approach for collecting sufficient data, however, is a laborious work because the transcription initiation involves multiple factors, and the principles of promoter actions are still too complex to be unraveled.

We have previously developed a new method [1] for automatically identifying possible regulatory signal patterns with optimal lengths from a set of unaligned sequences which are known to be functionally related but not all of which have common homologous regions. It takes the advantages of the Markov chain, relative entropy, and information content theories. Here we present a prediction method for expression specificity of promoters as an application of these extracted conserved patterns.

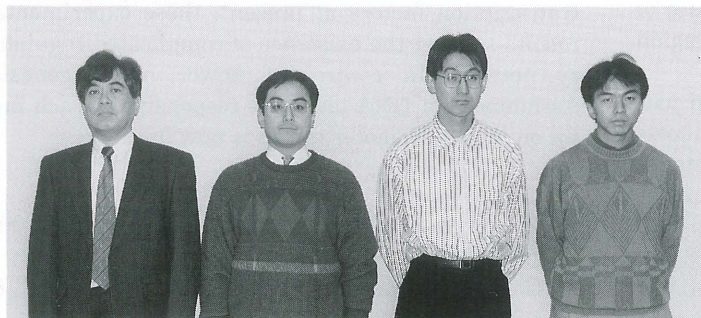
*Homo sapiens* promoters (-200 to -1) were collected from the EMBL nucleic acid database Release 41.0 according to the EPD [2] entries. We obtained 191 independent (non-homologous) promoters, including

## MOLECULAR BIOLOGY AND INFORMATION — Biological Information Science—

### Scope of research

*The following is the current major activities of this laboratory.*

- Characterization of amino acid sequence motifs from protein structure and sequence databases.
- Characterization of nucleotide sequence motifs around promoter, translation initiation and splice sites.
- Construction of new databases that describe molecular interactions, such as signal transduction and metabolic pathways.
- Modeling three-dimensional structures of RNAs, DNAs and proteins, and their interactions.
- Development of database systems and computational tools to support genome research. They are made freely available all over the world via the Internet (<http://www.genome.ad.jp/>).



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9, 36 and 20 active promoters in the brain, liver and house-keeping genes, respectively.

Conserved patterns were extracted based on the binomial distribution model, in which we can approximately calculate the probability  $P$  of finding a pattern  $K$  or more times. Given the number of sequences  $N$ , the probability  $p$  of finding a pattern in one sequence, and the ratio  $a = K/N$ , the following equation holds for  $0 < p < a < 1$ :

$$p \sim \frac{1}{1-r} \left( \frac{l}{\sqrt{2pa(1-a)N}} \right) e^{-NH}$$

where  $r = p(1-a)/[a(1-p)]$  [3], and  $H$  is the relative entropy between the observed frequency  $a$  and the expected frequency  $p$  calculated from the background nucleotides by assuming the first order Markov chain:

$$H = a \log(a/p) + (1-a) \log\{(1-a)/(1-p)\}.$$

Taking into account the various lengths of patterns, we have developed a method of defining sequence blocks by merging the fixed-length fragments (see [1] for detail) based on the information content theory.

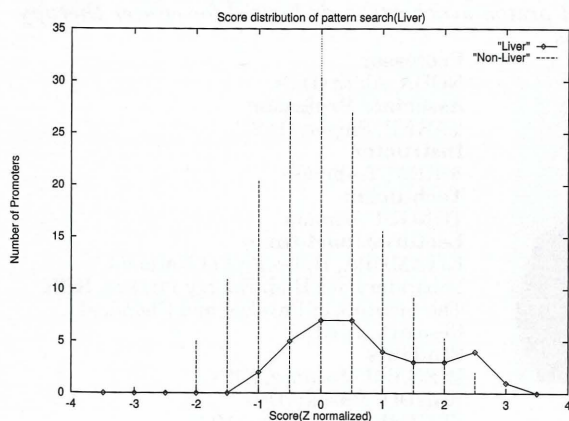
Once conserved block patterns for each promoter group are found, the degree of those specificities are determined by comparing relative conservation rate between the group and the outside of the group, which is defined by the index PSI [4]:

$$\text{PSI} = \log \frac{\text{const} + F_g}{\text{const} + F_r}$$

where  $F_g$  and  $F_r$  are, respectively, the fractions of sequences containing a pattern in a given group and in the rest of the groups.

In order to examine the predictive ability of this index, a test promoter is checked in turn whether it has any specificity by the following score, which is calculated from a set of indices defined from the rest of the promoters in the dataset.

$$\text{score} = \sum_{\text{found patterns}} \text{PSI}$$



**Figure 1.** The plot of score distribution profile for both liver and non-liver promoters.

**Table 1.** A Summary of total prediction rate for brain, liver and house-keeping gene promoter expression.

Promoter(#)	Correct Answer(%)	False Positive(%)
Brain(9)	44.4	16.1
Liver(36)	41.7	15.9
House-keeping(20)	50.0	11.6

The name of promoter group, the number of sequences, and the rates of both correct answers and false positives are shown. The values in the case where the threshold is set to be  $Z \geq 1.0$  are shown here.

Figure 1 is an example of score distributions for liver specific promoters and the rest of the promoters, which shows a difference in the two distribution profiles. If the threshold is set to be  $Z \geq 1.0$ , which can discriminate 41.7% of liver-specific promoters, the false positive rate is 15.9%. Note that the profile for the liver is spread wider, which may suggest that the liver-specific promoters can be divided into subgroups.

The summary of total prediction rate is shown in Table 1. The result also indicated that there was no gene preference for giving a correct answer (data not shown).

The PSI indices may give us an important clues for understanding biological processes. For example, it shows a pattern 'TGCCCA' is specifically conserved in the liver promoter group (~42% of the promoters). It closely resemble to the known consensus patterns of liver-specific factor ('TG[A/G][A/C]CC' and a portion of 'TGGTTATN[A/T]TCNNCA') in the TFD transcription factor database[5]. It is, however, still unregistered in the database.

As the genome sequencing projects proceed, there will be more pressing needs for understanding signals that may play important roles in gene regulation and expression. The method presented here is a step forward toward extracting and applying biological knowledge from rapidly expanding sequence data.

### Acknowledgment

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## Construction of 100 MeV Electron Linac

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An electron linear accelerator has been constructed as an injector of the storage ring. The output beam energy of the linac is 100 MeV and the designed beam current is 100 mA at the pulse width of 1  $\mu$ sec. The construction of the linac has been finished and we succeeded to accelerate the electron beam of 140 mA in October, 1995. The precise measurements of the beam parameters are now going.

**Keywords:** Linear Accelerator/ Synchrotron Radiation/ disc-loaded structure/ klystron

A compact electron storage ring (Kaken Storage Ring, KSR) and the linear accelerator are now under construction at the Institute for Chemical Research (1),(2). The layout of the accelerators is shown in Fig. 1. The maximum beam energy of the KSR is 300 MeV. It will be used as the synchrotron radiation source from the dipole magnet and the insertion device. The critical wave length is 17 nm.

The electron linac is composed of an electron gun, a buncher and three accelerating structures. The output beam energy is 100 MeV. It will be used for the beam injection to the KSR and the experiments using the 100 MeV electron beam.

The electron gun is a Pierce type gridded gun. The maximum extraction voltage is -100 kV. The phase spread of the beam is reduced by the pre-buncher and the buncher. The designed phase spread of is within 3 degree at the beam current of 100 mA when the input power is 12 MW. The main accelerating structure is a disc-loaded one and a traveling wave type. The electric

**Table 1.** Main parameters of the electron beam.

Energy	100 MeV
Beam Current	100 mA
Pulse Width	1 $\mu$ sec
Maximum Repetition	20 Hz

field is 45 MV per one accelerating structure without beam loading at the input power of 20 MW.

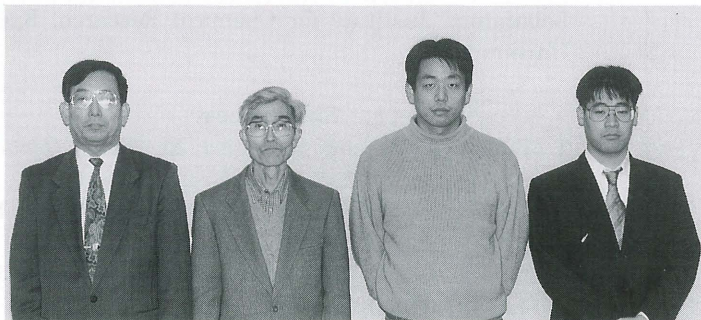
The RF frequency is 2857 MHz and the main RF amplifier is a klystron (ITT-8568). The maximum output power is 21 MW and the RF pulse width is 2  $\mu$ sec. The stabilized power supply for the klystron modulator is used to keep the klystron power and the output beam energy. The klystron voltage stability is less than  $3 \times 10^{-3}$ .

Figure 2 shows the input RF power of the third accelerating structure and the accelerated beam pulse. The RF power is 20 MW and the beam current is 140 mA.

## NUCLEAR SCIENCE RESEARCH FACILITY — Particle and Photon Beams —

### Scope of Research

Particle and photon beams generated with accelerators and their instrumentations both for fundamental research and practical applications are studied. The following subjects are being studied: beam dynamics related to the space charge force in the accelerators; beam handling during the injection and extraction processes of the accelerator ring; radiation mechanism of photon by electrons in the magnetic field; interactions in the few-nucleon systems; R&D to realize a compact proton synchrotron dedicated for cancer therapy; and irradiation of materials with particle and photon beams.



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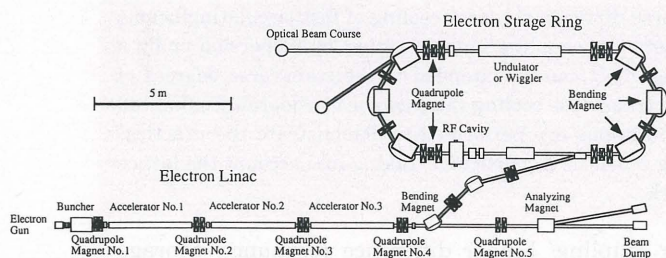


Figure 1. Layout of the linac and the KSR.

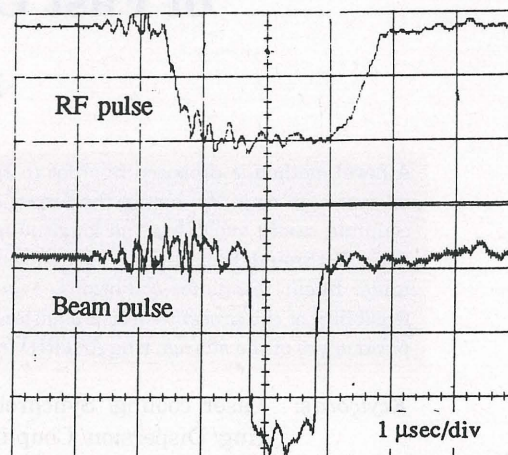


Figure 2. Input RF pulse of the third accelerating structure and the accelerated beam pulse.

## Quasifree-Scatterings and Quasifree-Reactions on Light Nuclei

Tadahiko Yoshimura and Shigeru Kakigi

The alpha cluster in a nucleus is expected to be softened compared with the alpha particle. To investigate experimentally the softening of the alpha cluster, it is desirable to measure the ratio of the cross section for the quasifree-scattering to that for the quasifree-reaction and to compare it with the corresponding ratio for the free processes.

**Keywords:** alpha cluster / Quasifree process

Alpha cluster structures have been studied both experimentally and theoretically and alpha clusters have been recognized to exist in many nuclei. This fact is due to the tight binding of the alpha particle with the binding energy of about 7 MeV/nucleon, large compared with neighboring nuclei. However, the alpha cluster in a nucleus is expected to be softened slightly through interactions with other nucleons surrounding the alpha cluster. An interesting problem arises: how much is the degree of the softening of the cluster.

The cluster structures of light nuclei have been investigated experimentally through quasifree processes at intermediate energies. In these processes, the projectile interacts directly with the alpha cluster in the target nucleus and the remaining part of it is playing as a spectator. In the quasifree-scattering (QFS), the projectile is quasi-elastically scattered from the alpha cluster. Another process is possible, that is the quasifree-reaction (QFR) [1], in which the collision of the projectile and the alpha cluster leads

to two-body rearrangement reactions. Experimentally it is desirable to measure the ratio of the cross section for the QFS to that for the QFR in order to cancel distortion effects. If the softening of the alpha cluster is assumed, the ratio for the quasifree processes is expected to decrease compared with the corresponding ratio for the free processes.

The experiments were performed with an 120 MeV alpha-particle beam and a 296 MeV proton beam from the AVF cyclotron and the ring cyclotron, respectively, at RCNP of Osaka University. The target nuclei were  ${}^6\text{Li}$ ,  ${}^7\text{Li}$ ,  ${}^9\text{Be}$  and  ${}^{12}\text{C}$ . Our preliminary results are suggesting the softening of the alpha cluster in  ${}^6\text{Li}$ . Further analyses are now in progress. The experiments were performed at RCNP in E46 and R04 collaborations.

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## Three-Dimensional Laser Cooling of Fast Circulating Beams

Hiromi Okamoto

A novel method is proposed in order to achieve three-dimensional laser cooling of fast circulating beams in a storage ring. We employ the forced synchrotron coupling induced either by dispersion or by a coupling cavity such that the longitudinal cooling effect can be extended to the transverse degrees of freedom through the coupling. It is shown that the transverse cooling rates can be considerably enhanced under linear resonance conditions. Tracking simulations are performed to demonstrate the practical feasibility of the present three-dimensional cooling schemes, in particular, taking into account the lattice parameters of the storage ring ASTRID in Denmark.

**Keywords:** Laser cooling/ Synchrotron coupling/ Linear difference resonance/ Storage ring/ Dispersion/ Coupling cavity

The laser cooling technique has been widely accepted, due to recent experimental success, as a powerful tool to manipulate the longitudinal phase space of stored and circulating ion beams. The beam temperature reachable with this new technique is now, at least, three orders of magnitude lower than that with the traditional techniques like electron cooling and stochastic cooling. In fact, the longitudinal temperature of 1 mK has been obtained in the ASTRID ring in Denmark with 100 keV  ${}^7\text{Li}^+$  beams. This is the main reason why laser cooling is often linked to the beam crystallization for which the beam temperature must be reduced to an extremely low level.

Contrary to this promising potential, laser cooling, if applied to beams in a storage ring, is essentially one-dimensional; namely, it operates only upon

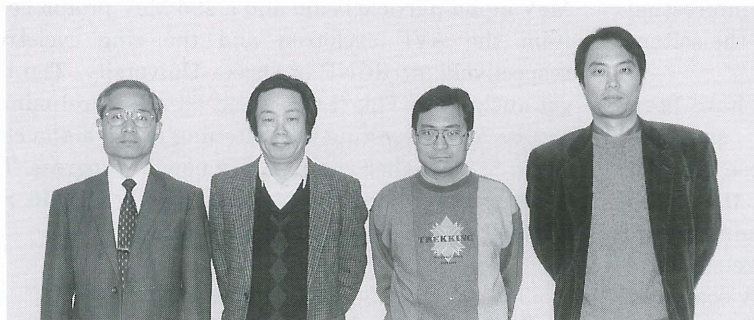
longitudinal motion. To overcome this difficulty, we proposed a novel method in the recent papers [1,2]. The idea is based on creating a linear synchrotron coupling such that the longitudinal damping action due to the laser cooling mechanism can be transferred into transverse directions. For this purpose, we developed two different schemes; namely, the dispersion-coupling scheme [1] and the coupling-cavity scheme [2].

In the first scheme, the synchrotron coupling induced through dispersion at an ordinary radio-frequency (RF) cavity was employed, while, in the second scheme, we introduced the so-called coupling cavity excited in a  $\text{TM}_{210}$  mode. It can be proven that these two schemes are mathematically almost equivalent and, therefore, work in a similar way. In the following, we only describe the first scheme since it is

### NUCLEAR SCIENCE RESEARCH FACILITY — Beams and Fundamental Reaction —

#### Scope of research

*Particle beams, accelerators and their applications are studied. Structure and reactions of fundamental substances are investigated through the interactions between beams and materials such as nuclear scattering. Tunable lasers are also applied to investigate the structure of unstable nuclei far from stability and to search for as yet unknown cosmological dark-matter particles in the Universe.*



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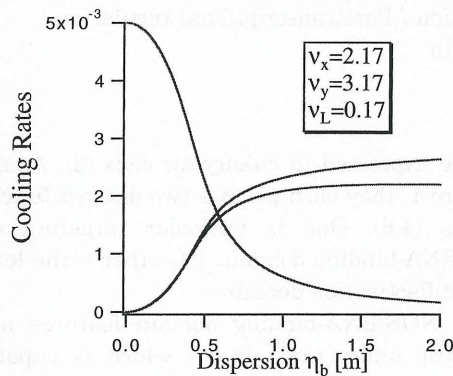


practically much simpler than the second scheme.

According to the theoretical predictions based on a linear model [1], the transverse cooling rates can be increased up to the same level as the longitudinal cooling rate, provided that the operating point of a storage ring is exactly on resonance; namely, when the conditions

$\nu_x - \nu_y = \text{integer}$ ,  $\nu_x - \nu_L = \text{integer}$ ,  
are satisfied (see Fig.1). Here,  $\nu_x$ ,  $\nu_y$ , and  $\nu_L$  are, respectively, the horizontal, vertical, and longitudinal tune. These conditions imply that the non-integer parts of the three tunes must be identical. Hence, it is required to set the longitudinal tune as large as possible to avoid the excitation of severe integer resonances in the transverse motions.

The easiest way to increase  $\nu_L$  is, indeed, the use of a higher RF voltage but it is clearly dangerous



**Figure 1.** The cooling rates of the horizontal, vertical, and longitudinal direction, under the resonance conditions, plotted as the function of the dispersion  $\eta_b$  at the RF-cavity position. Note that we have the optimum operating point where the three cooling rates are roughly the same. In this example, the optimum value of dispersion is clearly about 0.6 m.

since the longitudinal energy spread of laser-cooled beams eventually reaches even less than 0.1 eV. Further, recalling that the beam is initially continuous, we should adiabatically capture it first, ramping the RF voltage. This adiabatic capturing process causes the initial blowup of the longitudinal emittance where a larger bucket height results in a larger initial  $\delta p/p$  to be scanned. A lower RF voltage is thus preferable for shortening the cooling time as well. In ASTRID, the RF voltages of only 70 volts have actually been used for laser cooling experiments of bunched beams.

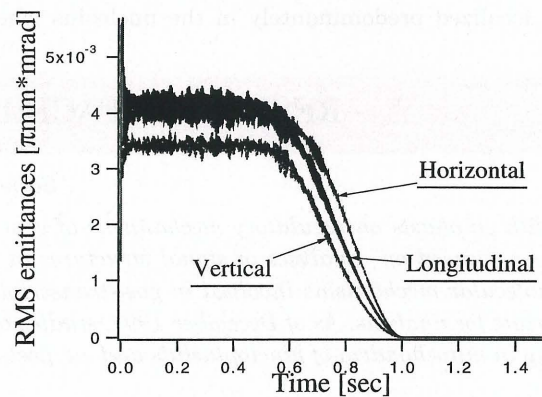
We now take a look at the result of a numerical simulation, confirming the validity of the proposed three-dimensional cooling method [3]. For this purpose, we here use the tracking code SIMPSONS originally written for the study of space-charge effects in synchrotrons. It is basically a thin-element code but enables us to do realistic investigation of the proposed cooling schemes with a specific lattice design.

Fig.2 shows the result where the exact lattice of the ASTRID ring has been considered, assuming 100 keV  $^{24}\text{Mg}^+$  beams initially continuous. Although  $\nu_x=2.29$  and  $\nu_y=2.73$  in the normal operating mode of ASTRID, the machine has been re-tuned here so that the coupling resonance conditions are satisfied; namely we have set the transverse tunes to be  $\nu_x=\nu_y=3.1$ . Further, an RF cavity is turned on to excite the synchrotron resonance. Employing the harmonic number  $h=260$  corresponding to 5.8 MHz, we only need 34 volts to obtain  $\nu_L=0.1$ .

We put a skew quadrupole at the opposite side of the laser cooling section. The strength of the skew field is of essential importance since the cooling rates of the three directions are altered depending on it. The optimum value of the skew field gradient in the present case is  $(L/B\rho) \cdot (\partial B/\partial y) \sim 0.055 \text{ [m}^{-1}\text{]}$  where  $L$  is the length of the magnet.

To adiabatically capture the beam into the RF bucket, the RF voltage is linearly increased from 0 to 34 volts in the first 10 milli-seconds. Then, the cooling laser is switched on and is scanned from  $\delta p/p \sim 7.5 \times 10^{-4}$  down to  $\delta p/p \sim 0$  within 0.99 second at a constant speed. The magnitude of a longitudinal momentum kick by a single laser photon is fixed at about  $\delta p/p \sim 1.5 \times 10^{-5}$  in the present simulation.

The result in Fig.2, perfectly consistent with the theoretical predictions, demonstrates the promising possibility of the proposed cooling method. We thus believe that, in order to approach closer to an ultimate limit of cold beams, the present three-dimensional cooling schemes should be tried.



**Figure 2.** Time evolutions of the RMS emittances of a laser-cooled beam.

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# Molecular Mechanism of Rev/Rex-Dependent *Trans*-Activation of Viral Genes

Yoshifumi Adachi

Rev of human immunodeficiency virus 1 (HIV-1) and Rex of human T-cell leukemia virus type I (HTLV-I) are post-transcriptional *trans*-activator proteins of viral gene expression. Rev and Rex are localized in the nucleolus and bind specifically to the Rev responsive element (RRE) and Rex responsive element (RxRE) sequences in viral RNAs. Furthermore, the interactions of Rev/Rex proteins with cellular cofactors are essential for Rev/Rex-dependent *trans*-activation *in vivo*. By means of affinity chromatography and biospecific interaction analysis, we identified 38-kDa nucleolar shuttle protein B23 and 18-kDa proteins (eukaryotic initiation factor 5A and prothymosin  $\alpha$ ) as the major proteins binding to the nucleolar localization signal/RNA-binding domain and leucine-motif/activation domain of Rev/Rex, respectively. Recently, nucleopolin-like proteins, Rab and Rip1p were also identified as the Rev/Rex activation domain-binding proteins. The functional relationship and molecular interaction between Rev/Rex, their binding proteins, and RRE/RxRE-containing viral RNAs are discussed.

**Keywords:** Retrovirus / HIV-1 / HTLV-I / Gene expression / Posttranscriptional regulation / Nucleolar localization signal / Shuttle protein

Rev of human immunodeficiency virus type 1 (HIV-1) and Rex of human T-cell leukemia virus type I (HTLV-I) (1) are novel post-transcriptional trans-activators. They are known to bind to their specific targets on viral unspliced (*gag-pol*) and partially spliced (*env*) mRNAs to enable the expression of viral structural proteins by accumulating these mRNAs to cytoplasm, hence they are critically required for viral transcription followed by replication (1-6). Besides having such a functional similarity, it has also been reported that both proteins are phosphorylated and are localized predominantly in the nucleolus when

they are expressed in eukaryotic cells (2). As shown in Figure 1, they each possess two distinct functional domains (4,6). One is nucleolar targeting signal (NOS)/RNA-binding domain. The other is the leucine-rich motif/activation domain.

The NOS/RNA-binding domain features a very long basic amino-acid stretch which is capable of forming an amphipathic  $\alpha$ -helix structure. The NOS/RNA-binding domain was shown to bind directly to the nucleolar protein B23 and the stem-bulge structure in the Rev/Rex responsive element (RRE/RxRE) of viral mRNAs (4). B23 has been shown

## RESEARCH FACILITY OF NUCLEIC ACIDS

### Scope of Research

*With emphasis on regulatory mechanisms of gene expression in higher organisms, the research activity has been focused on analyses of signal structures at the regulatory regions of transcriptional initiation and of molecular mechanisms involved in post-transcriptional modification by the use of eukaryotic systems appropriate for analysis. As of December 1994, studies are concentrated on the molecular mechanism of RNA editing in mitochondria of kinetoplastids and of post-transcriptional trans-activation of human retroviral genes.*



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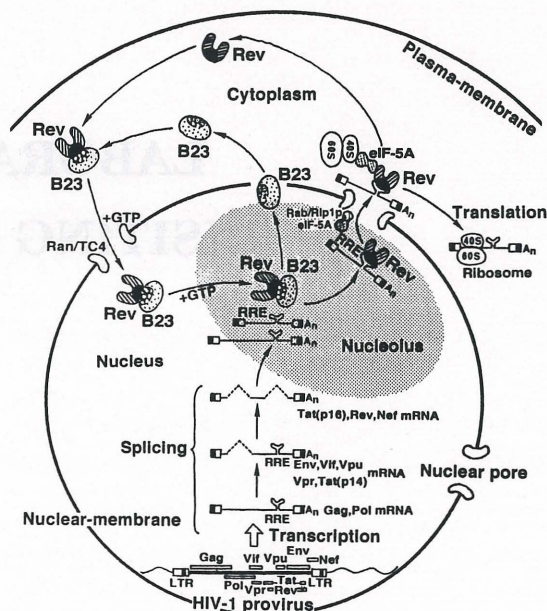
<b>HIV-1 Rev</b>	
1	MAGRSQSDSDLLKAV 34
17	RLIKFLYQSNPPNPEG <u>TRQARRNRNRNRWRERORQ</u> 51
	71 <u>VLQLPFLRLTLD</u> 90
	91 <u>TSQGTGVGSPQILVESPTIL</u> 110
	111 <u>ESGAGE</u> 116
<b>HTLV-I Rex</b>	
1	<u>MPKTRRRRPRRSORKRPPTP</u> 19
	41 <u>TVTKATGAPSLGDIYRPAIT</u> 60
	61 <u>VTPYWPVQSIIRSPGTFSD</u> 80
	81 <u>ALSAQLYSSLSLDS</u> 100
	101 <u>EPLRPSRSLPRQSLIQPPTF</u> 120
	121 <u>HPSSSRPCANTFPSEMDTN</u> 140
	141 <u>PFLGSTQPCLCFOTPDGFK</u> 160
	161 <u>TCTPSGEAPLSACTSTSTFP</u> 180
	181 <u>PSPGPSCPT</u> 189
<b>SIV Rev</b>	
	--- <u>TANQRRQRRRRWRRRWQ</u> ---
<b>HIV-1 Tat</b>	
	--- <u>RKKRRQRRRPQG</u> ---
<b>p120</b>	
	--- <u>SKRLSSRRARKRAAKRRLG</u> ---

**Figure 1.** Molecular structure of HIV-1 Rev, HTLV-I Rex, and related proteins. The wavy underlines indicate a basic, arginine-rich core which is essential for both the nucleolar localization and sequence-specific binding to the RRE/RxRE RNAs. The open boxes indicate a leucine-rich motif/activation domain which promotes the cytoplasmic transport of RRE/RxRE RNAs by interaction with specific cofactors. The circled P means *in vivo* phosphorylation site.

to migrate between the nucleolus and cytoplasm, acting as a shuttle protein for the nucleocytoplasmic transport of ribosomal components across the nuclear membrane. Rev and Rex utilize this shuttle service to be imported into the nucleolus as the Rev-B23 and Rex-B23 complexes via the NOS/RNA-binding domain. The RRE/RxRE RNAs having higher affinities for Rev/Rex than B23 are interesting in view of *in vivo* function of these interactions. Our findings suggest that the nucleolar-imported complexes formed by Rev/Rex and B23 are specifically dissociated by RRE/RxRE RNAs. The Rev-RRE/Rex-RxRE complexes replaced via NOS/RNA-binding domain may then be ready for the nuclear export machinery (Figure 2).

Mutational analysis has revealed that the leucine-rich motif/activation domains are also important for the complete functions of Rev/Rex (3). Interestingly, peptide core motifs within these domains are functionally interchangeable between Rev and Rex (1-4). These findings suggest that Rev and Rex should require common cellular cofactors involved in the cytoplasmic transport and/or accumulation of RRE/RxRE RNAs, which should interact through the activation domains. Recently, eukaryotic initiation factor 5A (eIF-5A), prothymosin  $\alpha$  (ProT $\alpha$ ) (6), nucleopolin-like proteins (Rab and Rip1p) were identified as the activation domain-binding proteins. These proteins are capable of binding to the activa-

tion domain when Rev and Rex assembled onto RRE/RxRE RNAs via NOS/RNA-binding domain and of significantly enhancing Rev/Rex-dependent *trans*-



**Figure 2.** Possible mechanism of Rev-dependent *trans*-activation of HIV-1 genes.

activation of viral genes. It seems possible that the subsequent interaction of the Rev-RRE/Rex-RxRE complexes with eIF-5A, ProT $\alpha$ , Rab or Rip1p via the activation domain may induce the nuclear export of the complexes across the nuclear pores followed by the preferential accumulation and translation of RRE/RxRE RNAs (Figure 2).

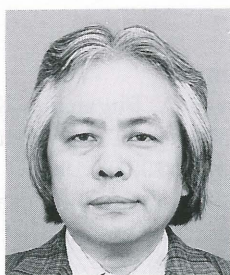
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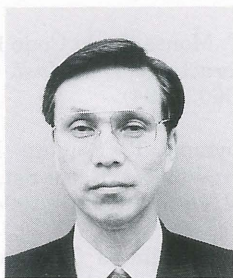
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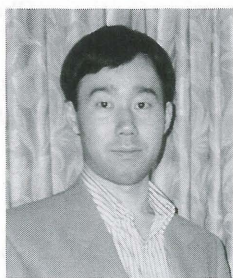
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Noda A, Inoue M, Iwashita Y, Shirai T, Nishi M, Hiramoto K and Hirota J: Design of a Compact Proton Accelerator Facility Dedicated for Cancer Therapy, *Proc. of the 10th Symposium on Accelerator Science and Technology, Hitachinaka, Japan*, 413-415 (1995)

Noda K, Minohara S, Torikoshi M, Kanazawa M, Takada E, Araki N, Noda A, Itano A, Sato K, Ogawa H and Yamada S: A Treatment Beam Control System for Irradiation Gated by Respiration of a Patient, *Proc.*

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Shirai T, Sugimura T, Kando M, Ikegami M, Iwashita Y, Okamoto H, Kakigi S, Dewa H, Tonguu H, Fujita H, Noda A, Mashiko K and Inoue M: 100 MeV Electron Linac in Kyoto University, *Proc. of the 20th Linear Accelerator Meeting, Osaka, Japan*, 13-15 (1995)

Noda A, Ikegami M, Inoue M, Iwashita Y, Okamoto H, Kakigi S, Kando M, Shirai S, Sugimura T, Dewa H, Tonguu H, Fujita H and Mashiko K: Electron Storage and Stretcher Ring, KSR, *Proc. of the 20th Linear Accelerator Meeting, Osaka, Japan*, 137-139 (1995)

Gluckstern R L, Okamoto H and Zotter B: Transverse Stability of Bunch Trains, *Phys. Rev.* **E52**, 1026-1038 (1995).

Matsuki S, Ogawa I, Nakamura S, Takimoto T and Okano K: DYNASP: A New Method to Measure Electromagnetic Moments of Unstable Nuclei by Polarizing after Implantation into a Semiconductor InP, in *Proceedings of the International Conference on Nuclear Shapes and Nuclear Structure at Low Excitation Energies, Antibes (France)*, 247-252 (1995)

Yamagata T, Utsunomiya H, Tanaka M, Nakayama S, Koori N, Tamii A, Fujita Y, Katori K, Inoue M, Fujiwara M, Ogata H: Elastic Scattering of  $^3\text{He}$  Particles at 450 MeV, *Nucl. Phys.*, **A589**, 425-434 (1995)

## RESEARCH FACILITY OF NUCLEIC ACIDS

Kubota S, Adachi Y, Copeland TD and Oroszlan S: Binding of Human Prothymosin a to the Leucine-motif/Activation Domains of HTLV-I Rex and HIV-1 Rev, *Eur. J. Biochem.*, **233**, 48-54 (1995)

Dr. Yuri Konstantinovich Batygin  
Moscow Engineering Physics Institute, Russia  
"Numerical Study of Low Energy Beam Transport and Acceleration"  
Thursday 26 January 1995



## SEMINARS

Dr. Yuri Konstantinovich Batygin  
Moscow Engineering Physics Institute, Russia  
"Nonlinear Beam Dynamics Effects in High Current Particle Accelerator"  
Friday 27 January 1995

Professor and Director Joachim Messing  
The Waksman Institute, Rutgers University,  
Piscataway, New Jersey, U.S.A.  
"Regulation of Gene Silencing during Reproduction and Development"  
Monday 30 January 1995

Professor Yoshishige Yamazaki  
National Laboratory for High Energy Physics, KEK  
"Present Status of the Accelerator Developments for Japanese Hadron Project"  
Tuesday 7 February 1995

Professor Kouji Hirata  
National Laboratory for High Energy Physics, KEK  
"Local and Global Approaches to the Equilibrium Envelope Calculation"  
Wednesday 15 February 1995

Prof. Chi-Huey Wong  
Scripps Research Institute, U.S.A.  
"Inhibition of Carbohydrate-Mediated Cell Adhesions"  
Friday 17 February 1995.

Professor Robert West  
Department of Chemistry, University of Wisconsin,  
Madison, USA  
"Stable Disilenes and Silylenes"  
Tuesday 21 February 1995

Associate Professor En-Tang Kang  
Department of Chemical Engineering, National University of Singapore  
"Surface Modification and Functionalization of Electroactive Polymers"  
Wednesday 8 March 1995

Associate Professor Peter Brick  
Imperial College University of London, UK  
"The structure of Lysyl t-RNA Synthetase"  
Monday 13 March 1995

Professor Tadashi Sugawara  
College of Arts and Sciences, University of Tokyo, Japan  
"Self-Assembly with Higher Functions of Organic Molecules"  
Wednesday 15 March 1995

Professor Toshiyuki Hattori  
Tokyo Institute of Technology, Japan  
"Study of IH-type Linear Accelerators for Application"  
Wednesday 22 March 1995

Dr. Alexander Bürkle  
Deutsches Krebsforschungszentrum, Heidelberg, Germany  
"Expression of Truncated and Full-Length Versions of Poly(ADP-ribose) Polymerase in Stably Transfected Cells; Biochemical and Biological Consequences"  
Thursday 6 April 1995

Prof. Upendra. K. Pandit  
University of Amsterdam, Netherland  
"Antitumor Alkaloids of Plant and Marine Origin. Synthetic Studies"  
Thursday 13 April 1995.

Prof. Yves Langlois  
Université de Paris-Sud, France  
"Progress in Alkaloids and Antibiotics Synthesis"  
Monday 17 April 1995.

Professor Dieter Vollhardt  
Max-Planck Institut für Kolloid- und Grenzflächenforschung, Berlin, Germany  
"Higher-Order Structures of Insoluble Monolayers at the Water Surface Studied by Brewster Angle Microscopy"  
Monday 24 April 1995

Dr. Yoshiaki Sohrin  
Institute for Chemical Research, Kyoto University  
"Polypyrazolyl: Analytical Chemistry by New Chelating Agents"  
Saturday 6 May 1995.

Professor K. Peter. C. Vollhardt  
Department of Chemistry, University of California, Berkeley, USA  
"Total Synthesis of Rather Unnatural Molecules: the Phenylenes"  
Monday 5 June 1995

Dr. M Engel  
Optical Information Materials Section, Hitachi Research Laboratory, Japan  
"Polymorphism in Phthalocyanines"  
Tuesday 6 June 1995

Professor Nitash Balsara  
Polytechnic University, New York, USA  
"Imperfections in Block Copolymer Structures"  
Friday 9 June 1995

Professor Yoshio Kitaoka  
Faculty of Engineering Science, Osaka University, Osaka, Japan  
"Progress in theoretical and experimental study of strongly correlated electron system I: NMR"  
Friday 16 June 1995

Professor Naoto Nagaosa  
Faculty of Engineering, University of Tokyo, Tokyo Japan  
"Progress in theoretical and experimental study of strongly correlated electron system II: Theory"  
Friday 16 June 1995

Professor Kazuyoshi Yamada  
Faculty of Science, Tohoku University, Sendai, Japan



"Progress in theoretical and experimental study of strongly correlated electron system III: Neutron Scattering"  
Friday 16 June 1995

Professor Michio Yamada  
Department of Mathematical Science, Graduate School of Science, University of Tokyo  
"Data Analysis by Wavelet"  
Friday 16 June 1995

Professor Reginald H. Mitchell  
Department of Chemistry, University of Victoria, Victoria, Canada  
"Synthetic Strategies for Making Unusual  $\pi$ -Systems"  
Monday 19 June 1995

Professor Takeshi Katayama  
Institute for Nuclear Study, University of Tokyo  
"Collider Ring Project for RI Beam Factory at RIKEN"  
Thursday 22 June 1995

Professor Takeshi Endo  
Research Laboratory of Resources Utilization, Tokyo Institute of Technology  
"Molecular Design of Functional Polymers on the basis of Organic Synthesis"  
Monday 8 July 1995

Professor Joanna Strosznajder  
Medical Research Laboratory, Polish Academy of Sciences, Warsaw, Poland  
"Molecular Mechanism of NO Action and Its Role in Brain Ischemia"  
Monday 10 July 1995

Professor J. J. Freire  
University of Complutense, Madrid, Spain  
"Monte Carlo Simulation of Hydrodynamic Interactions of Linear and Star Chains in Different Solvent Conditions"  
Thursday 13 July 1995

Professor Kobashi Kyoichi  
Toyama Medical and Pharmaceutical University, Faculty of Pharmaceutical Science, Japan  
"Usefulness and toxicity of urease : from sword bean to pyroli"  
Wednesday 20 July 1995

Prof. Nobuyuki Harada  
Institute of Chemical Reaction Sciences, Tohoku University  
"Recent Advances in CD Spectroscopy: Determination of Absolute Configuration by the Calculation of CD Spectra"  
Friday 28 July 1995.

Professor Hironari Yamada  
Faculty of Science and Engineering, Ritsumeikan University "Free Electron Laser with use of an Electron Storage Ring of Perfect Circular Shape"  
Friday 4 August 1995

Professor Theodore Friedmann  
Department of Pediatrics, University of California, San Diego, USA  
"Challenges and Opportunities in Human Gene Therapy"  
Monday 14 August 1995

Professor Zvi Rappoport  
Department of Organic Chemistry, Hebrew University of Jerusalem, Jerusalem, Israel  
"Stable Simple Enols"  
Tuesday 5 September 1995

Dr. D. D. Sarma  
Indian Institute of Science, Bangalore, India  
"Photoemission Study of Transition Metal Oxides"  
Friday 8 September 1995

Prof. Sun Handong  
Kunming Institute of Botany, China  
"Natural Product Chemistry of Plants in Yunnan"  
Monday 11 September 1995.

Professor Hideo Kitamura  
National Laboratory for High Energy Physics, KEK/The Institute of Physical and Chemical Research, RIKEN  
"Highly Brilliant Synchrotron Light Source"  
Tuesday and Wednesday 19 and 20 September 1995

Dr. Ludek Karasek  
Institute for Chemical Technology, Prague, Czech Republic  
"Polymer-Filler Interactions and Filler Distribution in Rubber-Carbon Black Systems"  
Wednesday 20 September 1995

Professor Xiuzhong Zhou  
Nankai University, P. R. China  
"Synthesis of  $(\text{Me}_2\text{M-MMe}_2)[\eta^5-(\text{C}_5\text{H}_3\text{R})\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$  and A Novel Reaction Between Their M-M and Fe-Fe Bonds (M = Si, Ge)"  
Friday 22 September 1995

Professor Klaus Hafner  
Institut für Organische Chemie, Technische Hochschule Darmstadt, Darmstadt, Germany  
"Recent Advances in the Chemistry of Carbocyclic  $\pi$ -Electron Systems; Their Transition Metal Complexes and Phanes"  
Monday 25 September 1995

Prof. Lewis N. Mander  
The Australian National University, Australia  
"Structural and Synthetic Studies on Novel Gibberellins from Fern Gametophytes and Apple Seeds"  
Tuesday 3 October 1995.

Dr. Bernard Badet and Marie - Ange Badet - Denisot  
Institut de Chimie des Substances Naturelles Centre National de la Recherche Scientifique Gif-sur-Yvette, France  
"The double life of glucosamine-6-phosphate synthase: mechanistic investigations of a peculiar glutamine-dependent amidotransferase"  
Monday 9 October 1995

Professor Klaus Baberschke  
Institut für Experimentalphysik, Freie Universität Berlin, Germany  
"The Magnetism of Nickel Monolayers"  
Thursday 10 October 1995

Professor David Rice and Dr. Patrick Baker  
Department of Molecular Biology and Biotechnology The University of Sheffield, UK



"Insights into the Catalysis, Specificity and Stability of the Amino Acid Dehydrogenase Superfamily"  
Friday 13 October 1995

Professor Takashi Yamauchi  
Department of Biochemistry, Faculty of  
Pharmacological Sciences, Tokushima University,  
Tokushima, Japan  
"Structure and Function of  $\text{Ca}^{2+}$ /Calmodulin-  
Dependent Protein Kinase II"  
Monday 16 October 1995

Professor Tadashi Asanuma  
Institute for Chemical Research, Kyoto University  
"Polymerization of  $\alpha$ -Olefins by means of Metallocene  
Catalysts"  
Thursday 19 October 1995

Dr. Monica Palcic  
Department of Chemistry Faculty of Science  
University of Alberta, Canada  
"Isotopic Probes of Amine Oxidase Reactions"  
Monday 23 October 1995

Dr. Alan R. Rein  
National Cancer Institute-Frederick Cancer Research  
and Development Center, Frederick, Maryland, USA  
"The Functions of Nucleocapsid Protein in Retrovirus  
Replication"  
Friday 27 October 1995

Professor J. M. Vergnaud  
Faculte de Science et Technique, Universite Saint-  
Etienne, France  
"Matter Transfers in Polymers: Theory and  
Applications"  
Monday 30 October 1995

Professor M. Yoon  
Department of Textile Engineering, Kon-kuk  
University, Seoul, Korea  
"Outline of Textile Industry and Textile Engineering  
Education in Korea"  
Wednesday 1 November 1995

Professor Maria Tomasz  
Department of Chemistry, The City University of New  
York, New York, U.S.A.  
"The Mitomycin Antitumor Antibiotics: Multiple Mode  
of Structural and Functional Modification of DNA"  
Monday 13 November 1995

Professor. Carl B. Collins  
University of Texas, U.S.A.  
"Gamma Ray Laser with Induced Gamma Radiation"  
Wednesday 15 November 1995

Professor Marek Janusz Wojcik  
Faculty of Chemistry, Jagiellonian University,  
Krakow, Poland  
"Dynamic Interaction in Hydrogen-Bonded Systems"  
Wednesday 15 November 1995

Prof. Ari. Mauri. P. Koskinen  
University of Oulu, Finland  
"Asymmetry -To Make a Distinction. Recent Studies  
in the Asymmetric Synthesis of Natural Products"  
Tuesday 21 November 1995.

Professor Jean-Francois Biellmann

University of Stasbourg, France  
"From Affinity Label to a Thiol Group Reagent"  
Wednesday 22 November 1995

Dr. Eberhard Keil  
SL Division, CERN, Switzerland  
"LEP Operation with Bunch Trains"  
Tuesday 28 November 1995

Professor Dr. Yasukiyo Ueda  
Faculty of Engineering, Kobe University, Japan  
"Functions and Structures of Organic Thin Films"  
Wednesday 29 November 1995

Dr. Ilme Schlichting  
Max Plank Institute for Molecular Physiology,  
Dortmund, Germany  
"Watching a Protein at Work: Kinetic X-Ray  
Crystallography on Myoglobin-CO"  
Wednesday 29 November 1995

Professor Peter M. Levy  
Department of Physics, New York University, New  
York, USA  
"Giant Magnetoresistance in Metallic Multilayers"  
Thursday 30 November 1995

Professor Manron B. Salamon  
Department of Physics, Illinois University, Urbana,  
IL, USA  
"Thermopower and Thermal Conductivity in GMR  
Materials"  
Monday 4 December 1995

Professor Moshe Gottlieb  
Ben Grion University, Beer Sheva, Israel  
"Rheological Studies on Red Microalgae  
Polysaccharide"  
Monday 4 December 1995

Professor Elizabeth C. Theil  
Department of Biochemistry & Physics, North  
Carolina State University, Raleigh, U.S.A.  
"Transition Metal Complexes and NMR Spectroscopy  
as Probes of the IRE (Iron Regulatory Element)  
Structure in Ferritin mRNA"  
Thursday 7 December 1995

Assistant Professor Detlef Weigel  
Plant Biology Laboratory, The Salk Institute for  
Biological Studies, La Jolla, California, U.S.A.  
"Initiation and Patterning of Flowers in *Arabidopsis*"  
Monday 11 December 1995

Associate Professor June Medford  
Department of Biology and Biotechnology Institute,  
The Pennsylvania State University, Philadelphia,  
Pennsylvania, U.S.A.  
"Positional Controls of Pattern Formation in  
*Arabidopsis*"  
Monday 11 December 1995

Professor Timothy P. Lodge  
University of Minnesota, Minneapolis, USA  
"Recent Results on the Structure and Phase Behavior  
of Block Copolymer Liquids"  
Tuesday 12 December 1995

Professor Matthew Tirrell  
University of Minnesota, Minneapolis, USA



**"Shear Effects on Block Copolymers near the Order - Disorder Transition"**

Tuesday 12 December 1995

Professor Ihn Kyo Jin  
Kangwon National University, Korea  
"Crystallization Behavior of Poly(3-alkylthiophene)  
Molecules on Polyethylene Crystals"  
Friday 15 December 1995

Professor Narayan Bhattacharya  
National Laboratory for High Energy Physics (Visiting

Prof.) and  
Variable Energy Cyclotron Center,  
Department Atomic Energy, Calcutta, India  
"The Superconducting Cyclotron Project at Calcutta"  
Monday 18 December 1995

Prof. Shiro Ikegami  
Faculty of Pharmaceutical Sciences, Teikyo University  
"New Synthetic Reactions Utilizing Organolead  
Reagents"  
Thursday 21 December 1995.



# MEETINGS AND SYMPOSIUMS

## ICR ANNUAL MEETING 1995

December 8, 1995

### I. Oral Presentations

(Wood Composites Hall, Wood Research Institute,  
Kyoto University, Uji, Kyoto-fu)

1. Properties and Catalytic Mechanism of 2-Haloacid Dehalogenases  
Esaki N, Kurihara T, Liu J, Soda K, Hisano T, Fujii T and Hata Y
2. Reduction of  $\alpha$ -Ketoesters by Bakers' Yeast in an Organic Solvent.  
Nakamura K, Kondo S, and Ohno A
3. Long-Range Density Fluctuations in Amorphous Polymers  
Kanaya T and Kaji K
4. Ion-channels Formed by Peptides in Bilayer Lipid Membranes  
Koji Asami
5. NMR Analysis of Aggregation and Hydration Structure of a Photosynthesis Pigment  
Okamura E, Wakai C, and Nakahara M
6. Preparation and Properties of Artificial Superlattices of High- $T_c$  Superconductors  
Terashima T and Bando Y
7. Spin Ladder Materials: High pressure synthesis, crystal structure and physical properties  
Takano M

### II. Posters

(5th Floor Large Meeting Room, Institute for  
Chemical Research, Kyoto University, Uji, Kyoto-fu)

1. Electron Energy Loss Spectra of 3d Transition Metal Phthalocyanines.  
Koshino M., Kurata H., Isoda S. and Kobayashi T
2. Structure and Growth of Ultra Thin Hexadecachloro Phthalocyanine Copper Film.  
Irie S., Hosino A., Isoda S. and Kobayashi T
3. Dependence of the Amount of Stacking Faults in Syndiotactic Polystyrene Single Crystals on the Crystallization/Annealing Temperature  
Hamada N, Tosaka M, Tsuji M and Kohjiya S
4. Nanometer Scale Structure of Organic/Inorganic Hybrid Gels by the Sol-Gel Process  
Hirata Y, Tsuji M, Kohjiya S, Ikeda Y, Urakawa H and Kajiwaru K
5. Solid-state Phase Transformation in the Drawing Process of Poly(tetramethylene succinate)

Tsujimoto J, Murakami S, Tsuji M and Kohjiya S

6. Dynamical NMR Study on the Effect of Solvent, Temperature, and Pressure on the Translational and Rotational Diffusion of Water Molecules  
Wakai C and Nakahara M
7. Ultra Trace Elements in the Southern Ocean  
Iwamoto S, Sohrin Y and Matsui M
8. Design of Highly Selective Solvent Extraction Systems Utilizing Macrocyclic Compounds as a Masking Reagent  
Sasaki T, Umetani S and Matsui M
9. Arsenic in Lake Biwa  
Sohrin Y, Tateishi T and Matsui M
10. Molecular Design of Organic Ligands of High Selectivity for Metal Ions : Effect of the Distance between Two Donating Oxygens and the Intramolecular Interaction  
Le T H Q, Umetani S and Matsui M
11. Magnetoresistance Effect of Metallic Multilayers Grown on Microstructured Substrates  
Ono T, Sugita Y, Shigeto K and Shinjo T
12. Magnetic Polarization of Au in Co/Au and Fe/Au Metallic Multilayers Investigated by Sn Probe Layers  
Emoto T, Hosoi N and Shinjo T
13. Preparation of Bi-2201 Phase with stoichiometric composition of cations under 1 atm. of oxygen  
Niinae T, Ikeda Y and Bando Y
14. Magnetism and Electric conductivity of  $\text{SrRuO}_3/\text{SrTiO}_3$  artificial superlattices  
Izumi M and Bando Y
15. Electric Field Effects in Ultrathin  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  Films  
Komai E, Nakazawa K, Terashima T and Bando Y
16. Phase Diagram of  $\text{NdO}_{1.5}\text{-SrO-CuO}$  System  
Yamada T, Niinae T, Ikeda Y and Bando Y
17. Crystal Growth and Superconductivity of Pb Substituted Bi-2201 Phase  
Chong I, Terashima T, Ikeda N, Bando Y and Takano M
18. Carrier doping to New oxygen deficient perovskite compounds.  $(\text{Ln}, \text{Sr})\text{CuO}_{2.5}$   $\text{Ln}=\text{La}, \text{Pr}, \text{Nd}$   
Kobayashi N, Hiroi Z and Takano M
19. Crystal Structure and Superconductivity of  $(\text{Hg}, \text{Re}) \text{Sr}_2\text{Can-1CuO}_y$  ( $n=2, 3$ )



- Yamaura K, Poulsen J, Hiroi Z, Takano M, Shimoyama J and Kishio K
20. Ferromagnetism of Perovskite  $\text{AFe}_{1-x}\text{Co}_x\text{O}_3$  (A=Sr, Ca)  
Kawasaki S and Takano M
  21. Nonlinear Optical Properties of Borate Glasses Containing p-Block Elements  
Terashima K, Hashimoto T, Uchino T and Yoko T
  22. Dynamics of Styrene-Isoprene-Styrene Triblock Copolymer Dissolved in a Selective Solvent: Rubbery-Plastic-Viscous Transition and Dielectric Relaxation.  
Sato T, Watanabe H and Osaki K
  23. Viscoelasticity of Polystyrene around the Glass Transition Zone. On the Effect of Plasticizer.  
Mizukami Y, Inoue T and Osaki K
  24. Stress Relaxation Mechanism of Polymers around the Glass Transition Zone.  
Matsui H, Inoue T and Osaki K
  25. Small-Angle Neutron Scattering from Polyelectrolyte Solutions  
Shibano T, Nishida K, Kanaya T and Kaji K
  26. Viscosity of Charged Spherical Particles.  
Kiriya K, Nishida K, Kanaya T, Kaji K and T Okubo\* (\* Dept Polym Chem, Kyoto Univ)
  27. Thermodynamic and Hydrodynamic Second and Third Virial Coefficients of Poly( $\alpha$ -methylstyrene) in Benzene  
Tsunashima Y
  28. TEM Study on Formation Process of Microfibrils of Bacterial Cellulose  
Hirai A, Tsuji M, Horii F and Yamamoto H
  29. Solid-state  $^{13}\text{C}$  NMR Analyses of the Structure and Molecular Motion of the Polyurethane Sample Crystallized from the Liquid Crystalline State  
Ishida H, Kaji H and Horii F
  30. New Polymeric Materials Synthesized by "Living" Radical Polymerization Using Stable Nitroxide Radicals  
Terauchi T, Fukuda T, Tsujii Y and Miyamoto T
  31. Structural Studies on Langmuir-Blodgett Films of Amphiphilic Block Copolymer Having Glucose Residues  
Yamamoto S, Yamada K, Tsujii Y, Minoda M, Fukuda T and Miyamoto T
  32. Synthesis of  $\text{C}_{60}$ -End-capped Polymers  
Okamura H, Minoda M, Miyamoto T and Komatsu K
  33. Synthesis and Properties of Macrocyclic  $\pi$ -Conjugated Systems Having Rigid Bicyclic  $\sigma$ -Frameworks  
Nishinaga T, Kawamura T and Komatsu K
  34. Acid-Catalyzed Carbonylation of Chlorine-Substituted Aldehydes - Steric Control of the Cyclization Products by Acid Strength  
Mori S, Emura K, Kano M, Kudo K, Komatsu K and Sugita N
  35. Regioselective Inclusion of a Fluoride Ion in Silicon-Based Linear Multi-Nuclear Lewis Acids  
Sun G-R, Kawachi A, Tamao K
  36. Electronic Structure of Silole: Important Role of  $\sigma^*-\pi^*$  Conjugation  
Yamaguchi S, Tamao K
  37. A New Efficient Method for the Preparation of Allene Carboxylate by the Reaction of BHT esters with the HWE Reagent.  
Ohtsubo K, Tanaka K and Fuji K
  38. Asymmetric Reduction with Enzymes.  
Kawai Y
  39. Stereochemistry in Oxidoreduction of Nicotinamide Analogs.  
Yamazaki N
  40. Synthesis of Optically Active  $\alpha$ -Arylethanol by Microbial Transformation Using *Geotrichum candidum*.  
Nakamura K, Matsuda T, Inoue Y, and Ohno A
  41. Structural Analysis of DNA-C1027 Chromophore Complex by NMR Method  
Okuno Y and Sugiura Y
  42. Distribution of Joining Peptide in Rat Brain  
Hamakubo T.
  43. Possible Mechanism of Nucleolar Translocation and Activation of HIV-1 Rev and HTLV-I Rex  
Adachi Y, Ueda K
  44. LipB, Lipase Activator Protein - Reactivation of Lipase with Amino-Terminal Truncated Mutants  
Shibata H, Kato H and Oda J
  45. Catalytic Mechanism of Fluoroacetate Dehalogenase  
Kurihara T, Liu J, Ichiyama S, Esaki N and Soda K
  46. Stereochemistry of Proton Transfer Catalyzed by Pyridoxal Enzymes and Their Molecular Evolution  
Yoshimura T, Jhee K, Esaki N and Soda K
  47. The Characteristic Structure and Molecular Evolution of Thermoacidophilic Archaeal Ferredoxin  
Fujii T and Hata Y



48. Structure-Based Functional Properties of L-2-Haloacid Dehalogenase  
Hisano T, Hata Y, Fujii T, Liu J-Q,  
Kurihara T, Esaki N and Soda K
49. Study of Space Charge Effects in High Intensity Ion Beam with one-dimensional PIC Simulation  
Ikegami M
50. Present Status of 100 MeV Electron Linear Accelerator at ICR  
Sugimura T, Inoue M, Noda A, Kakigi S,  
Iwashita Y, Okamoto H and Shirai T

## ICR Symposium 1995

June 15, 1995

(Kyodai-Kaikan, Kyoto University, Kyoto)

1. Dynamical NMR of Water and Aqueous Solutions under Extreme Conditions  
Nakahara M
2. Frontier Studies on New Materials Research  
Shinjo T
3. Application of Neutron Scattering to Polymer Science  
Kaji K
4. The Ultimate Microanalysis Aiming at a Single Atom Analysis by Electron Microscopy.  
Kobayashi T
5. Information Analysis of Genes and Genomes: Deciphering Mysteries of Life  
Kanehisa M
6. Analysis of the mechanism of protein function - glutathione synthetase as an example of analysis -  
Oda J

## SYMPOSIUMS ORGANIZED BY RESEARCH FACILITY OF NUCLEIC ACIDS

### SYMPOSIUM ON

"Technical Problems in Genome Projects"  
Friday, January 20, 1995

"A High Resolution Physical Map of the Human Chromosome 21"  
Dr. Eiichi Soeda  
Tsukuba Life Science Center, Institute of Physical and Chemical Research (RIKEN), Tsukuba, Japan

"C. elegans cDNA Projects"  
Associate Professor Yuji Kohara  
National Institute of Genetics, Mishima, Japan

"Computer Analysis of DNA Sequences and its Application in Rice Genome Research"  
Dr. Akio Miyao

Rice Genome Research Program, National Institute of Agrobiological Resources, Tsukuba, Japan

"Integration of Genome Databases"  
Professor Toshihisa Takagi  
Human Genome Center, Institute of Medical Science, The University of Tokyo, Tokyo, Japan

"Learning Algorithms"  
Professor Satoru Miyano  
Research Institute of Fundamental Information Science, Faculty of Science, Kyushu University, Fukuoka, Japan

"On the Possibility of Biological Researches by Computer Simulation"  
Associate Professor Masami Hagiya  
Graduate School of Science, The University of Tokyo, Tokyo Japan

### WORKSHOP ON

"*Arabidopsis thaliana*"

Thursday, 9 November 1995

Friday, 10 November 1995

"Database of Molecular Biology of *Arabidopsis thaliana*"  
Dr. Nobuaki Hayashida  
Tsukuba Life Science Center, Institute of Physical and Chemical Research (RIKEN), Tsukuba, Japan

"Signal Transduction through Protein Kinases"  
Dr. Akira Usami  
Department of Biology, Faculty of Science, Nagoya University, Nagoya, Japan

"Signal Transduction Responsive to Light Stimulus"  
Dr. Minami Matsui  
Institute of Physical and Chemical Research (RIKEN), Wako, Japan

"Transfer of and Response to Nutritional Information in Higher Plants"  
Dr. Tohru Fujiwara  
Faculty of Agriculture, The University of Tokyo, Tokyo, Japan

"Signal Transduction Pathway Induced by Desiccation"  
Dr. Kazuo Shinozaki  
Tsukuba Life Science Center, Institute of Physical and Chemical Research (RIKEN), Tsukuba, Japan

"Transcriptional Control of the Genes for Seed Storage Proteins"  
Professor Satoshi Naito  
Faculty of Agriculture, Hokkaido University, Sapporo, Japan

### TECHNICAL PRACTICE

"Genetic Analysis of *Arabidopsis* Mutants"  
Professor Satoshi Naito  
Faculty of Agriculture, Hokkaido University, Sapporo,



Japan  
Dr. Tohru Fujiwara  
Faculty of Agriculture, The University of Tokyo,  
Tokyo, Japan  
Dr. Nobuaki Hayashida  
Tsukuba Life Science Center, Institute of Physical and  
Chemical Research (RIKEN), Tsukuba, Japan

"Signal Transduction Analysis with Transgenic Plants"  
Dr. Minami Matsui  
Institute of Physical and Chemical Research (RIKEN),  
Wako, Japan  
Dr. Kazuo Shinozaki

Tsukuba Life Science Center, Institute of Physical and  
Chemical Research (RIKEN), Tsukuba, Japan  
Dr. Akira Usami  
Department of Biology, Faculty of Science, Nagoya  
University, Nagoya, Japan

#### ENLIGHTENMENT PROGRAM

Experiencing Course (organized in collaboration with  
Division of Molecular Biology and Information)  
"The Forefront of Research on Biological Science:  
Instruction and Practice"  
Saturday 24 June 1995 and Saturday 1 July 1995



# THESES

HWANG, Eui-Jeong  
D Eng, Kyoto University  
"Dynamic Birefringence and Viscoelasticity of Amorphous Polymer in the Glass Transition Zone"  
Supervisor: Professor Osaki K  
23 November 1994

SUZUKI, Mitsuko  
D Sc, Kyoto University  
"Ion Transfer from Water to Formamide, 1,2-Ethanediol or the Mixture of Formamide and Water Studied by Voltammetry for Ion Transfer at the Liquid/Liquid Interface"  
Supervisor: Professor Matsui M  
23 January 1995

ITOH, Shigeki  
D Agr, Kyoto University  
"Microbial Transformation of Oleic Acid and Stearic Acid"  
Supervisor: Professor Soda K  
23 January 1995

BAKTHAVATSALAM, Sundararaju  
D Agr, Kyoto University  
"Structure and Function of Thermostable and Halotolerant Leucine Dehydrogenases"  
Supervisor: Professor Soda K  
23 January 1995

LIU, Ji-Quan  
D Agr, Kyoto University  
"Structure and Function of Bacterial L-2-Halo Acid Dehalogenase"  
Supervisor: Professor Soda K  
23 February 1995

SHIMURA, Kenichi  
D Sc, Kyoto University  
"Study of Microstructures and Superconductivity of Ultrathin  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  Films"  
Supervisor: Professor Bando Y  
23 March 1995

FUJIHARA, Shinobu  
D. Eng, Kyoto University  
"Studies on the Synthesis, Properties and Chemical Modification of Superconducting Oxides"  
Supervisor: Professor Yoko T  
23 March 1995

HASHINMOTO, Tadanori  
D. Eng, Kyoto University  
"Studies on Third-Order Nonlinear Optical Properties of Transition Metal Oxide Thin Films Prepared by Sol-Gel Method"  
Supervisor: Professor Yoko T  
23 March 1995

OKAMOTO, Hirotaka  
D Eng, Kyoto University  
"Studies of Relaxation in Solid Polymers by Dynamic Mechanical and Birefringence Measurements"  
Supervisor: Professor Osaki K  
23 March 1995

TAKADA Akihiko

D Eng, Kyoto University  
"Thermotropic Liquid Crystals of Cellulose and Cellooligosaccharide Derivatives"  
Supervisor : Professor Miyamoto T  
23 March 1995

KONDO Shin-ichi  
D Sci, Kyoto University  
"Stereochemical Control in Microbial Reduction "  
Supervisor: Prof. A. Ohno  
23 March 1995

MARUYAMA Tetsushi  
D Sci, Kyoto University  
"Diaminotetracarboxylate-Type Chelators: Synthesis, Structure, and Selectivity for Affinity to Metal Ions"  
Supervisor: Prof. A. Ohno  
23 March 1995

UESUGI, Motonari  
D Pharm Sc, Kyoto University  
"Studies on DNA Recognition and Strand Scission by Antitumor Antibiotics, Esperamicin  $\text{A}_1$  and Elsamicin A"  
Supervisor : Professor Sugiura Y  
23 March 1995

OGIWARA, Atsushi  
D Sci, Kyoto University  
"Construction and Analysis of a Profile Library Characterizing Groups of Structurally Known Proteins"  
Supervisor: Professor Kanehisa M  
23 March 1995

SUYAMA, Mikita  
D Agr, Kyoto University  
"Searching for evolutionary relationships among functionally related enzymes"  
Supervisor : Professor J.Oda  
23 May, 1995

TCHORZEWSKI, Marek  
D Agr, Kyoto University  
"Structure and Function of Nitroalkane Oxidizing Flavoenzymes"  
Supervisor: Professor Soda K  
23 May 1995

NAGAI, Atsuko  
D Agr, Kyoto University  
"Enzymological and Molecular Biological Studies of Cabbage Histidinol Dehydrogenase"  
Supervisor: Professor Soda K  
23 May 1995

DAIJIRO, Hagiwara  
D Pharm Sc, Institute for Chemical Research Kyoto University  
"Studies on the Antagonist of Substance P Having Di-And Tripeptide Structure"  
Supervisor: Prof. Kaoru Fuji  
23 May 1995

Bo, Li  
D Pharm Sc, Institute for Chemical Research Kyoto University



"Studies on New Diterpenoids form Taxus Species in China"

Supervisor: Prof. Kaoru Fuji

23 May 1995

NISHIYAMA, Hiroko

D Agr, Kyoto University

"Enzymological Characterization and Application of Aliphatic Amino Acid Dehydrogenases"

Supervisor: Professor Soda K

24 July 1995

AZUMA, Masaki

D Sc, Kyoto University

"High Pressure Synthesis of Cupric Oxides Having Quantum Spin Properties"

Supervisor: Professor Takano M

25 September 1995

ZHAO, Gaoling

D. Eng, Zhejian University (China)

"Sol-Gel Preparation and Optical and Photoelectrochemical Properties of Oxide Composite Films Containing Metal Nanoparticles"

Supervisor: Professor Yoko T

23 November 1995

SUGIURA Makoto

D Eng, Kyoto University

"Discotic Liquid Crystals Based on Chito- and Cello-oligosaccharides"

Supervisor : Professor Miyamoto T

24 November 1995

NARDI-DEI, Vincenzo

D Agr, Kyoto University

"L- and DL-2-Halo Acid Dehalogenases from Pseudomonas Bacteria: Structures and Catalytic Functions"

Supervisor: Professor Soda K

24 November 1995

WATANABE, Mutsumi

D Agr, Kyoto University

"Breeding of Sake Yeast and Its Brewing Properties"

Supervisor: Professor Soda K

24 November 1995

ONDA, Masaaki

D Agr, Kyoto University

"Molecular Genetics of Glycophorin A Gene Family"

Supervisor: Professor Soda K

24 November 1995



INSTITUTE FOR CHEMICAL RESEARCH  
KYOTO UNIVERSITY

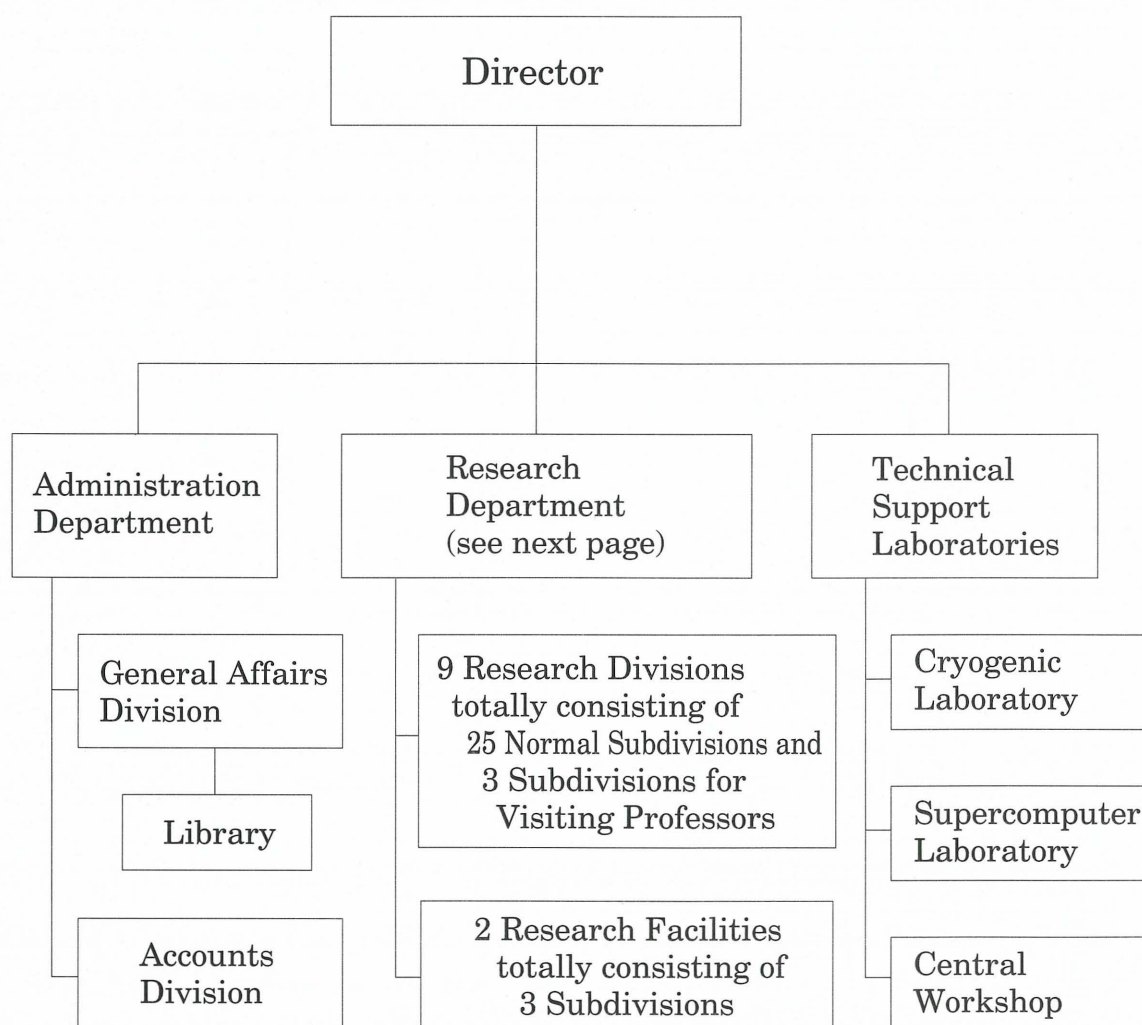
## ORGANIZATION AND STAFF

Director





INSTITUTE FOR CHEMICAL RESEARCH  
KYOTO UNIVERSITY





Director  
MIYAMOTO, Takeaki

Research Division	Subdivision(Laboratory)	Related Graduate School < Graduate School of / Division of >	Professor	Associate Professor	Instructor
States and Structure	I . Atomic and Molecular Physics	< Science / Physics I >	MUKOYAMA, Takeshi	ISOZUMI, Yasuhito	KATANO, Rintarou ITO, Yoshiaki NAKAMATSU, Hirohide
	II . Crystal Information Analysis	< Science / Chemistry >	KOBAYASHI, Takashi	ISODA, Seiji	KURATA, Hiroki OGAWA, Tetsuya
	III . Polymer Condensed States Analysis	< Engineering / Polymer Chemistry >	KOHJIYA, Shinzo	TSUJI, Masaki	URAYAMA, Kenji TOSAKA, Masatoshi MATSUMOTO, Mutsuo
Interface Science	I . Solutions and Interfaces	< Science / Chemistry >	NAKAHARA, Masaru	UMEMURA, Junzo	KIMURA, Noriyuki MATSUBAYASHI, Nobuyuki
	II . Molecular Aggregates	< Science / Chemistry >	SATO, Naoki	ASAMI, Koji	KITA, Yasuo SEKINE, Katsuhisa
	III . Separation Chemistry	< Science / Chemistry >	MATSUI, Masakazu	UMETANI, Shigeo	SASAKI, Yoshihiro SOHRIN, Yoshiki
Solid State Chemistry	I . Artificial Lattice Alloys	< Science / Chemistry >	SHINJO, Teruya	HOSOITO, Nobuyoshi	MIBU, Ko
	II . Artificial Lattice Compounds	< Science / Chemistry >	BANDO, Yoshichika		IKEDA, Yasunori TERASHIMA, Takahito
	III . Multicomponent Materials	< Science / Chemistry >	TAKANO, Mikio	HIROI, Zenji	AZUMA, Masaki
	IV . Amorphous Materials	< Engineering / Molecular Engineering >	YOKO, Toshinobu	KOZUKA, Hiromitsu	UCHINO, Takashi
Fundamental Material Properties	G. Structure Analysis		TERAUCHI, Hikaru	TAKAGI, Hidenori	
	I . Molecular Rheology	< Engineering / Molecular Engineering >	OSAKI, Kunihiro	WATANABE, Hiroshi	INOUE, Tadashi
	II . Polymer Materials Science	< Engineering / Polymer Chemistry >	KAJI, Keisuke	KANAYA, Toshiji	NISHIDA, Koji
	III . Molecular Motion Analysis	< Engineering / Molecular Engineering >	HORII, Fumitaka	TSUNASHIMA, Yoshisuke	KAJI, Hironori
	G. Composite Material Properties		MASAMOTO, Junzo	ASANUMA, Tadashi	
Organic Materials Chemistry	I . Polymeric Materials	< Engineering / Polymer Chemistry >	MIYAMOTO, Takeaki	FUKUDA, Takeshi	TSUJII, Yoshinobu MINODA, Masahiko
	II . High-Pressure Organic Chemistry	< Engineering / Energy & HC Chemistry >	KOMATSU, Koichi		MORI, Sadayuki KUDO, Kiyoshi NISINAGA, Tohru
Synthetic Organic Chemistry	I . Synthetic Design	< Engineering / Energy & HC Chemistry >	TAMAO, Kohei	TOSHIMITSU, Akio	KAWACHI, Atsushi YAMAGUCHI, Shigehiro
	II . Fine Organic Synthesis	< Pharmaceutical Sci. / Pharmac. Chem. >	FUJI, Kaoru	TANAKA, Kiyoshi	KAWABATA, Takeo
	G. Synthetic Theory		IKEGAMI, Shiro	KOBAYASHI, Shu	
Bioorganic Chemistry	I . Bioorganic Reaction Theory	< Science / Chemistry >	OHNO, Atsuyoshi	NAKAMURA, Kaoru	KAWAI, Yasushi
	II . Bioactive Chemistry	< Pharmaceutical Sci. / Drug System >	SUGIURA, Yukio	OTSUKA, Masami	MORII, Takashi
	III . Molecular Clinical Chemistry	< Medicine / Internal Medicine >	UEDA, Kunihiro		HAMAKUBO, Takao
Molecular Biofunction	I . Functional Molecular Conversion	< Agriculture / Agricul. Chem. >	ODA, Jun'ichi	NISHIOKA, Takaaki	KATO, Hiroaki HIRATAKE, Jun TANAKA, Takuji
	II . Molecular Microbial Science	< Agriculture / Agricul. Chem. >	SODA, Kenji	ESAKI, Nobuyoshi	YOSHIMURA, Tohru KURIHARA, Tatsuo
Molecular Biology and Information	I . Biopolymer Structure	< Science / Biophysics >	TAKAHASHI, Sho	HATA, Yasuo	HIRAGI, Yuzuru FUJII, Tomomi
	II . Molecular Biology	< Science / Biophysics >	OKA, Atsuhiro	AOYAMA, Takashi	GOTO, Koji
	III . Biological Information Science	< Science / Biophysics >	KANEHISA, Minoru	AKIYAMA, Yutaka	GOTO, Susumu FUJIBUCHI, Wataru
Nuclear Science Research Facility	I . Particle and Photon Beams	< Science / Physics II >	NODA, Akira	KAKIGI, Shigeru	SHIRAI, Toshiyuki
	II . Beams and Fundamental Reaction	< Science / Physics II >	INOUE, Makoto	MATSUKI, Seishi	IWASHITA, Yoshihisa OKAMOTO, Hiromi
Nucleic Acid Research Facility		< Science / Biophysics >		SUGISAKI, Hiroyuki	ADACHI, Yoshifumi

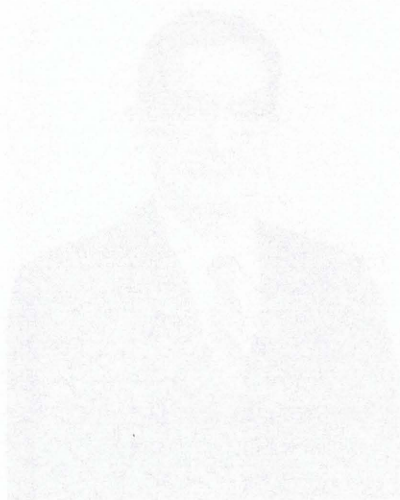






Professor Nobuyuki SUGITA

# PERSONAL



High-Pressure Organic Chemistry Laboratory

Division of Organic Materials

On the day of March 1977, Dr. Nobuyuki Sugita retired from Kyoto University after 37 years of service. In the meantime, he was honored with the title of Professor Emeritus of Kyoto University.

The center was born in the spring of the year 1940. At that time, Sugita was in the Department of Chemistry, Kyoto University, as an assistant professor. He had been working in the field of organic chemistry, particularly in the area of high-pressure organic chemistry, since 1935. He was one of the pioneers in this field in Japan.

In 1940, Sugita was appointed as an assistant professor in the Department of Chemistry, Kyoto University. He was promoted to professor in 1945. In 1948, he was appointed as the head of the High-Pressure Organic Chemistry Laboratory, which was then part of the Department of Chemistry, Kyoto University.

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In 1990, Sugita was appointed as the head of the High-Pressure Organic Chemistry Laboratory, which was then part of the Department of Chemistry, Kyoto University. He was promoted to professor in 1995. In 1998, he was appointed as the head of the High-Pressure Organic Chemistry Laboratory, which was then part of the Department of Chemistry, Kyoto University.

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## Retirement

### Professor Nobuyuki SUGITA

(High-Pressure Organic Chemistry Laboratory,  
Division of Organic Materials Chemistry)



On the 31st of March, 1995, Dr. Nobuyuki Sugita retired from Kyoto University after 37 years of service to the University, and was honored with the title of Professor Emeritus of Kyoto University.

Dr. Sugita was born in Hiroshima on the 26th of April, 1931. After graduation from the Department of Chemistry, Kyoto University, in 1955, he continued his study on high pressure chemistry as a graduate student at the Department of Fuel Chemistry, Kyoto University. In 1958, he was appointed an instructor of the Institute for Chemical Research, Kyoto University, under the supervision of Professor Emeritus Yoshimasa Takezaki. After receiving a doctoral degree from Kyoto University in 1966, he was promoted to an Associate Professor in 1967. On a leave of absence in the year 1976 to 1977, he worked on transition-metal catalysis under high pressure in cooperation with Professor R. F. Heck at the University of Delaware. In 1982, Dr. Sugita was appointed full Professor to direct the Division II of Organic Material Chemistry in this Institute. At the Division of Energy and Hydrocarbon Chemistry, Kyoto University, he gave lectures on high-pressure chemistry to graduate students.

His contribution to the Institute through both academic and administrative activities is hereby gratefully acknowledged, and his academic achievements are briefly described below.

Dr. Sugita's work has been concerned with high-pressure chemistry covering a wide area ranging from fundamental to applied chemistry. Also, throughout his study he has dealt with the so-called "C<sub>1</sub> chemistry," that is the effective transformation of carbon monoxide and dioxide which are abundant raw materials and the economical use of which is today's important issue from the viewpoint of environmental protection.

First to be mentioned of his contribution in these fields are the mechanistic study of carbonylation reactions utilizing various types of catalysts and its application. For acid-catalyzed reactions, he developed new synthetic methods in fuming sulfuric acid media. His detailed investigation on the use of HF/BF<sub>3</sub> catalyst system upon formylation of aromatic compounds was successfully applied to the industrial use. As an example of the base-catalyzed reactions, his novel method of malonic acid synthesis from potassium acetate in alkali-metal molten-salt media remarkably improved the efficiency of this reaction.

Dr. Sugita's extensive work on transition-metal catalyzed carbonylation reactions is noteworthy. He utilized an originally-designed IR cell, durable to high pressure and high temperature, for the in-situ observation of reactive intermediates as well as active catalyst. Dr. Sugita applied this method to develop various types of new carbonylation reactions and to clarify their mechanisms.

Another subject which Dr. Sugita devoted his effort was the activation and conversion of carbon dioxide into higher organic molecules. He obtained remarkable results regarding the carboxylation of amines and alcohols under pressurized carbon dioxide and hydrogen by the use of a rhodium catalyst. He also verified the presence of a carbon dioxide-organic base complex as a key intermediate in carbonylation of ketones and carboxylic acids. One of his recent results to be noted is the cesium carbonate-catalyzed synthesis of oxalic acid salt from carbon monoxide and dioxide.

Thus, through his study Dr. Sugita has shown us an ideal direction of the academic research that the successful application can be attained only by a thorough understanding of the fundamental phenomena. This principle will remain as a firm basis underlying the research work in the Institute.



## Retirement

### Professor Kenji SODA

(Molecular Microbial Science Laboratory,  
Division of Molecular Biofunction)



Dr. Kenji Soda, Professor of Microbial Biochemistry retired as a Professor Emeritus on the 31st of March, 1996 after having completed his 35 years of service at Kyoto University.

Dr. Soda was born in Aichi Prefecture on February 7, 1933. He graduated from Faculty of Agricultural and Biological Chemistry, Kyoto University in 1956 and continued his studies on microbial biochemistry under the supervision of the late Professor H. Katagiri. He graduated from the Doctor Course of Agricultural and Biological Chemistry, Kyoto University, and was awarded the degree of Ph.D. in 1961.

He started academic carrier as an instructor of the Department of Agricultural and Biological Chemistry, Kyoto University to study microbial biochemistry and biotechnology with the late Professor K. Ogata, and Professor T. Tochikura in 1962. During 1963 and 1965, on leave from Kyoto University he stayed at Tufts University School of Medicine, Boston, Mass, U.S.A. as a visiting research fellow of Department of Biochemistry, and studied the biochemistry of amino acids with Professor A. Meister. In 1965, he was promoted to Associate Professor at the Laboratory of Microbial Biochemistry of the Institute for Chemical Research, Kyoto University. In 1981, Dr. Soda was appointed full Professor of Kyoto University, and directed the Laboratory of Microbial Biochemistry, Institute for Chemical Research. At the Graduate School of Agriculture, Kyoto University, he gave lectures on Microbial Biochemistry and Applied Microbiology and supervised the dissertation works of many graduate students.

Dr. Soda devoted himself to the Japanese Biochemical Society and officiated as President of the Society between 1992 and 1993. He was also the trustee of Japan Society of Bioscience, Biotechnology and Agrochemistry, Vitamin Society of Japan, and others. He was awarded the Prize of Agricultural Chemical Society of Japan for Young Scientists in

1969, the Prize of Vitamin Society of Japan in 1985, and the Prize of the Japan Society of Bioscience, Biotechnology and Agrochemistry in 1992.

He is also known as an alpinist. He was the president of Mountaineering Club of Kyoto University, and is the trustee of Academic Alpine Club of Kyoto.

For the past forty years, he extensively investigated various aspects of microbial biochemistry. He studied the structure and functions of biocatalysts produced by microorganisms, in particular, pyridoxal enzymes, NAD enzymes, and flavin enzymes: he characterized L-lysine  $\epsilon$ -aminotransferase, D-amino acid aminotransferase, kynurenine aminotransferase, arginine racemase, alanine racemase, amino acid racemase with low substrate specificity, methionine  $\gamma$ -lyase, leucine dehydrogenase, alanine dehydrogenase, phenylalanine dehydrogenase, meso- $\alpha$ ,  $\epsilon$ -diaminopimelate D-dehydrogenase and others. He also carried out the research on the metabolism and biofunction of selenium-containing amino acids and peptides. He has found new enzymes participating in the selenium metabolism such as selenocysteine  $\beta$ -lyase and a new pathway of the microbial fluorine metabolism. He synthesized and characterized novel selenium-peptides serving as an antioxidant such as glutaselenone. He also engaged himself in the characterization and application of new biomolecules. For example, he has elucidated the molecular structure and functions of thermostable and thermolabile enzymes and studied their application. He established efficient systems for the enantioselective amino acid production with these enzymes. He discovered and characterized a few halo acid dehalogenases, and studied their structure and functions as well as new oxygenases and oxidases acting on nitro compounds. He modified and improved their properties by protein engineering and developed a new procedure to effectively decompose the nitro compounds in waste water by means of these enzymes.



## Obituary

### Professor Emeritus Dr. Eiji SUIITO (1912-1995)



Professor Dr. Eiji SUIITO, the ex-director of the Institute for Chemical Research, Professor Emeritus of Kyoto University and Professor Emeritus of Maizuru National College of Technology, and an Honorary Member of the Japanese Society of Electron Microscopy, suddenly passed away on July 6, 1995 in Kyoto.

He was born on January 23, 1912 in Kobe. After graduating from Kyoto University in March, 1936, with a degree in chemistry, as a graduate student he continued to study the chemical kinetics under the supervision of the late Professor Emeritus Shinkichi Horiba at the Department of Chemistry, the Faculty of Science, Kyoto University. He was conferred a D. Sc. by Kyoto University for his studies on colloid catalysis by thermal analysis.

Professor Suito was appointed an instructor at the Faculty of Science, Kyoto University in April, 1942, and joined the Institute for Chemical Research, Kyoto University, in May of the same year. He was appointed an Assistant Professor in November, 1945, and simultaneously became a full member of the Institute for Chemical Research. He was promoted to full Professor of the Institute in May, 1951, to direct the Laboratory of Crystal and Powder Chemistry. He introduced an electron microscope to his laboratory for the study of colloidal particles and fine powders. He gave lectures on crystal chemistry from 1965 at the Graduate School of Science, and supervised the dissertation works of many graduate students.

He was a visiting instructor at several universities including the Kyoto University of Industrial Arts and Textile Science (Kyoto Institute of Technology), Kobe

University, Okayama University, Kumamoto University, Kagoshima University and Tokushima University.

Two years after he was appointed the Director of the Institute in April, 1972, Professor Suito made substantial and enthusiastic contributions to enhance and develop the Institute. He served as a member of the University Council and various committees on the campus and greatly contributed to the university administration. After retiring from Kyoto University, he served as president of Maizuru National College of Technology for 10 years.

For six years beginning in 1966, he played an important role as a member of the Science Council of Japan for the promotion of scientific research. He also served as Vice President of the Chemical Society of Japan, President of the Japanese Society of Electron Microscopy, President of the Clay Science Society of Japan, and as a member of the Board of Directors of many scientific societies. He was awarded the prize from the Chemical Society of Japan in 1970 for his physico-chemical studies on colloid and fine powder as well as the Seto Prize from the Japanese Society of Electron Microscopy in 1957. In addition, he was awarded prizes of many other scientific societies. His ability to develop research work was frequently recognized. He was a member of many international organizing committees. Professor Suito visited many foreign countries to attend various international congresses. His stimulating papers always attracted the interest of the audience. He was awarded a Purple Ribbon Medal in 1977 and the Rising Sun Order with Double Stars in 1988.



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